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A POROUS PLUG METHOD FOR THE MECHANICAL EQUIVALENT OF HEAT.

By J. R. Roebuck.

"POROUS plug" is the term applied to experiments like those of Joule and Thompson, where a fluid moves along a tube through a porous obstruction, thereby suffering changes in pressure and in temperature. The initial and final pressures and the initial temperature are usually fixed by the experimenter and the final temperature allowed to adjust itself. In their work as with most of the later workers, the fluid moved along a tube past a thermometer, then through the porous plug, across which therefore there is a drop in pressure, and then past a second thermometer. During the passage through the plug the total energy does not change but it is redistributed. In the case of a liquid the pressure does work against friction in the pores, changing potential (PV) energy into heat, producing when undisturbed a rise in temperature. But the process is usually complicated by a change in temperature due to the change in volume following the change in pressure. When this latter temperature change can be made small and accurately measurable by other means, the change of mechanical energy into heat offers a promising means for the determination of the mechanical equivalent of heat. As compared with Rowland's method it has the advantages of continuous flow experiments where states usually transitory become steady ones and may be investigated at leisure.

Other observers have noted its advantages, among them Maxwell (Theory of Heat) who gives a mathematical treatment of the case. It has even been tried experimentally but so far as the writer is aware without publication. The unmanageable radiation and conduction losses of the forms of porous plugs hitherto employed would have presented great difficulty. The actual measurements required are limited to the determination of a difference of pressure and a difference of temper-

ature with some definitely determinable corrections which may be made small. The temperature difference across the plug is independent of the rate of flow if there are no heat losses, but depends upon the specific heat of the fluid. A liquid of low specific heat like mercury offers an advantage in the larger temperature difference obtained, but this is offset by the use of water to define the calorie and the accuracy with which the temperature variation of the specific heat of water is known. A liquid is to be preferred to a gas on account of the larger change in PV across the plug due to its small change in volume, which latter also eliminates changes of momentum if the cross sectional areas of flow past the thermometers are similar. Moreover the negative coefficient of expansion of water near the freezing point offers a means of eliminating experimentally the only serious correction. These considerations combined with its cheapness and ready purification lead to the choice of water as the working fluid.

THEORY.

The internal energy of a body is partly kinetic and partly potential, of which only the first part affects the temperature. Change in external pressure on a fluid by affecting the volume will usually cause a shift in the division of energy between the two forms, thus producing a change in the temperature. For the use of the porous plug process as a method of determining the relation between the heat energy produced and the work done upon the fluid, it is necessary to separate this temperature change due to internal energy rearrangements on the relief of pressure, from the temperature change due to the addition of energy in the form of work but which appears in the form of heat. This could be most directly accomplished by carrying out an adiabatic free expansion and a porous plug experiment between the same pressure limits at the same initial temperature. The adiabatic free expansion offers experimental difficulties which have been avoided by the use of a reversible adiabatic expansion. Tamman's (Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen) work on the reversible adiabatic expansion of water has shown that by a suitable choice of initial temperature and initial and final pressures, the final temperature may be made identical with the initial. The employment of these special conditions leads to a marked improvement in the experimental accuracy by limiting the measured temperature change to almost exactly that due to the work done upon the fluid.

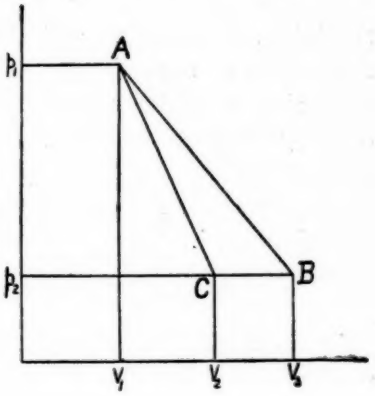
In the diagram let the point A represent the initial conditions of pressure, volume, and temperature and the point C the final. Substitute for the actual irreversible porous plug path AC, the reversible path

ABC, where AB is a reversible adiabatic expansion and BC the addition of heat at constant pressure. Then since the final states are the same,

$$\int_{ABC} du = \int_{AC} du = -\Delta(pv)$$

and

$$\int_{ABC} du = \int_{AB} du + J\int_B^C C_p dt - p_2(v_2 - v_3).$$



For the reversible adiabatic AB

$$\int_{AB} (du + pdv) = 0$$

or

$$\int_{AB} du = -\int_{AB} pdv.$$

Hence

$$-\Delta(pv)_{AC} = -\int_A^B pdv + J\int_B^C C_p dt - p_2(v_2 - v_3).$$

But as shown possible by Tamman's work, T_1, p_1 and p_2 are so chosen that B is on the same isothermal as A, that is T_1. For the particular series of experiments reported here v_2 and v_3 are equal as determined from the data on the coefficient of expansion of water. Computation shows that the term $\int_A^B pdv$ is only about 0.1 per cent. of the term $J\int_B^C C_p dt$ so that

$$\int_A^B pdv = \tfrac{1}{2}(p_2 + p_1)(v_2 - v_1)$$

may be taken as a sufficiently close approximation especially in view of the small size and constancy of the coefficient of compression. So that calling C the mean value in mechanical units between the temperatures T_1 and T_2, we have

$$(p_1v_1 - p_2v_2) = -\tfrac{1}{2}(p_2 + p_1)(v_2 - v_1) + C(T_2 - T_1)$$

or

$$C = \frac{\Delta p(v_1 + v_2)}{2\Delta T},$$

which is the expression used for the reduction of the experimental data. v_1 and v_2 are the specific volumes of the water at p_1T_1 and p_2T_2 respec-

tively, and their values are taken from Landolt's tables. This leaves two quantities to be measured, a difference of temperature and a difference of pressure. Experimentally this required the careful regulation of the initial temperature and the initial pressure. Electrical resistance thermometers were chosen as probably the most accurate means for measuring small differences of temperature and similarly an open tube mercury manometer for the pressure difference. The manageable mercury column limited the pressure difference to about 33 kg/cm^2 and this in turn fixed the temperature difference at about 0.76° C. under the conditions used. The apparatus is described in the following paragraphs.

PUMP.

As the required condition of steady small delivery at high pressure was not found in any commercially made pump, one was designed by the writer for this work and was built by Mr. Foerst, the department mechanician. It is a six plunger-piston pump, with the cylinders all connected in parallel, and all driven from a common crank shaft. The circular spacing of the cranks is in two groups of three each spaced at 120° with a phase difference between the groups of 30°. This phase difference was chosen because the theoretical delivery of three plunger pistons set at 120° gives six maxima and six minima. The second group is thus so set as to give the maxima of delivery coinciding with the minima of the first group. This gives a theoretical delivery varying only 4 per cent. with a frequency of 12 per revolution. In practice the setting of the conical hard rubber valves and the compression of the water in the cylinders probably introduced greater variation than this, though it was smoothed off considerably before reaching the plug by the elasticity of the system of tubes and the inertia of the water. A large Schaffer and Budenberg spring test gauge was connected to the plug chamber and under good working conditions it showed nothing but a barely readable variation per crank shaft cycle. In any case the variations being rapidly cyclic would be integrated similarly by the thermometer and by the manometer. The power was transmitted from the motor by a round belt to a bicycle wheel minus its rubber tire and from there through sprocket wheels and a chain to the crank shaft of the pump. It made a very reliable, cheap, and quiet method of speed reduction.

PRESSURE REGULATOR.

The pressure was controlled by regulating the speed of the D. C. shunt wound motor driving the pump. The apparatus is shown in diagram in Fig. 1. An accurately ground glass-hard steel piston rod

stands vertically in a leather-packed stuffing box in a heavy steel cylinder which is connected at its lower end directly to the plug chamber while at the stuffing box end it is filled with castor oil. This piston rod is arranged to rotate without rotating the load of sand and the latter is hung on gimbals to keep it centered. The piston is driven by a round belt from a parallel cylinder thus avoiding any component of the belt tension along its axis. To the load tank are attached 10 loops of high resistance wire connected in series with the armature of the motor. These loops dip into tubes filled with mercury and are supported independently of the tank. If the delivery of the pump was too great the piston rose, throwing resistance into the armature circuit and slowing the motor till the speed fell to the required delivery. While the piston was rising or falling with noticeable speed the pressure rose or fell slightly. Careful tests showed that the pressure was identical whether the piston came to position from above or below. During the readings the conditions were so steady that the piston did not shift more than a centimeter or two an hour and this shift was always a rise due to the slow clogging of the porous plug.

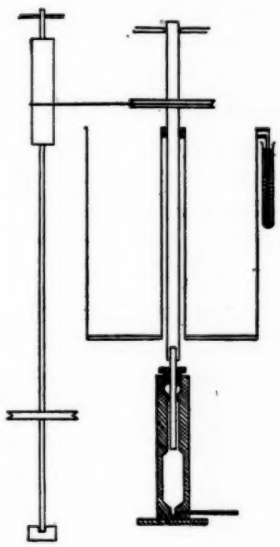


Fig. 1.

Manometer.

A mercury in glass[1] open-tube manometer was built following closely the design of Kammerling Onnes[2] except that water was used to separate the mercury surfaces,[3] and that the cathetometer arrangements were different. The general plan is a set of U-tubes connected in series, the lower halves filled with mercury and the upper with water. The mercury was carefully purified, and distilled water used both here and in the flow work. The difference in level of the mercury surfaces in each of the series of eight U-tubes was read on an invar tape suspended on a track just in front of the tubes. It was kept vertical and straight by a weight, which dipping in oil damped the swinging. The tape was divided accurately into millimeters on the department dividing engine by scratching in wax

[1] Physical Review, 28, 264, 1909.

[2] Proc. Amsterdam Acad., 1, 213, 1898 and 8, 75, 1905.

[3] Cf. Thiesen, Zeit. f. Instrumentkunde, p. 114, 1881.

and etching in acid. This division was compared on a Geneva comparator with the standard invar meter bar just returned from the Bureau of Standards; the correction was small, 13 parts per 100,000 and constant over the tape. For making the readings Professor Mendenhall suggested the use of two mirrors set at 45° to the vertical to avoid the difficulty of getting in line with the mercury surfaces near the ceiling or near the floor. Optical mirrors were required and they were carried on sliding supports on a steel bar set in bearings in the ceiling and floor. The central mirror rotated about a horizontal axis to reflect the image from either the upper or lower mirror into the telescope placed just behind it. All the supports were provided with the necessary motions and carefully adjusted. The base of the pillar was carried on the end of a millimeter micrometer screw provided with gear for adjusting by the operator in a standing position. Readings were made by moving the tape near to the tube, setting the cross hairs on the mercury meniscus, rotating the pillar till the tape replaced the mercury in the field, reading to the nearest millimeter on the tape and the fraction of the millimeter by shifting the pillar with the micrometer screw. The temperature of the mercury columns was determined by five thermometers hung in the manometer case. The large temperature difference between ceiling and floor occurring in a steam-heated room was reduced to about a degree by a fan-driven circulating system carrying the hotter air from the top and delivering it at the bottom of the case.

The manometer was tested by adjusting the levels to balance the pressure due to the loaded regulator, then the load was increased or decreased for a short time and replaced at its old value. The mercury meniscus always returned to its previous position to a part in 10,000 of the total mercury column. The actual pressure given by the regulator was dependent on the temperature of the steel piston and on the hygroscopic condition of the wooden base of the load tank so that it varied from time to time. Where more than one setting was made on the same day, the readings rarely differed by 0.1 per cent.

THERMOSTAT TANK AND PLUG.

The water delivered under steady pressure by the pump was led through 20 meters of copper tubing immersed in a large tank of water, the details of which are shown in Fig. 2. The tank had a separate inner compartment also stirred but containing no heater. The temperature was controlled by a large toluene thermostat provided with a Gowy regulator, which threw a heating current on and off 8 32-c.-p. lamps. The Gowy[1]

[1] Jour. de Physique, 6, 479, 1897.

regulator consists of an excentric for moving the mercury contact maker up and down 1–2 mm. in the thermostat capillary with a period of from 15–30 seconds. The result is that the mercury surface sets itself in the capillary so that the fraction of the period for which the heating current

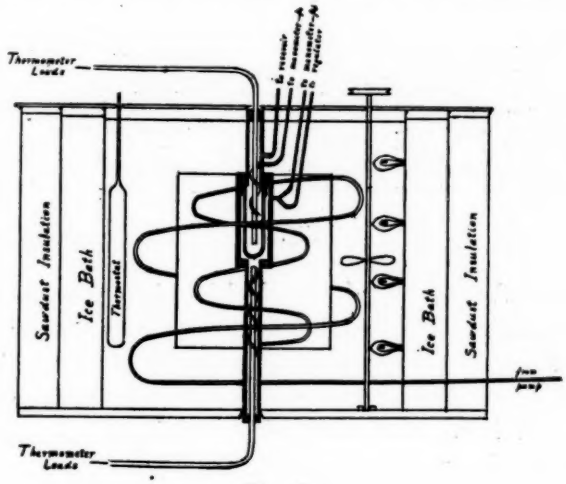


Fig. 2.

is on the lamps is sufficient to maintain the temperature constant. This eliminates most successfully all the "hunting" of the ordinary thermostat, making it unnecessary for any appreciable quantity of heat to flow into or out of the thermostat bulb. It was found possible to hold the temperature of the plug chamber constant to 2–3 ten-thousandths of a degree for an hour or more. For reasons to be given later it was advantageous to work between 3° C. and 4° C. and to this end the main bath was surrounded by another forming an annular space which was filled with ice and water. This was protected again by a box with sawdust insulation and the temperature could be readily maintained anywhere between 1.5° C. and 5° C.

Placed axially in the center of the set of tanks was a steel cylinder containing the thermometers and the plug. The water entered this tube from the copper tube at the lower end, passed spirally about the coil part of the platinum thermometer, radially through the plug, spirally about the second thermometer, and on to the reservoir above the pump. From this steel tube small copper tubes led the pressure to the regulator and to the upper and lower sides of the manometer. The arrangements inside the plug are shown in Fig. 3. The plug itself was made of porous porcelain tubing, some with round porous ends and others with flat nonporous ends. The theory of such a porous plug is discussed in an

earlier paper by Earl S. Burnett and the author.[1] Since this paper appeared my attention has been called to the fact that Regnault used such a porous plug, which was not known to us at the time. Regnault however says nothing about its protective features but discarded the arrangement and regretted the time put upon it. In the present case

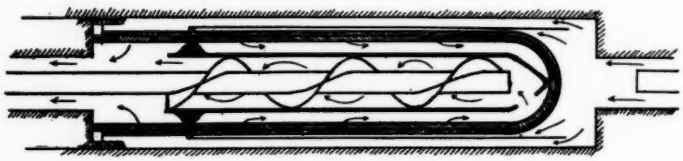


Fig. 3.

the water passes through the plug wall with a rise of temperature. Conduction losses might take place through the walls or through its support. In the former case the heat could only escape to the liquid just entering the wall and hence such conductivity could not be the cause of any continuous heat loss. Radiation might produce a continuous loss if the walls of the plug were at a different temperature from the walls of the container. In cases like this where the temperature gradient is opposed to the flow of the fluid, conductivity outward will be opposed by the flow, and the result will be a slight displacement outward of the temperature distribution. With sufficient flow the rise of temperature of the outer surface will be negligible. This can be rendered still more certain by providing a layer on the outside of the plug nonconducting and sufficiently porous to cause no appreciable pressure drop. This was the more necessary in the present case as the pores of the porcelain filled slowly with a deposit even though pure distilled water was used, and consequently a large part of the pressure drop took place close to the outside of the plug wall. To provide this layer and also to lessen the clogging of the wall, the outside of the plug was always covered with 8 or 10 layers of filter paper and 4 or 5 layers of cotton cloth. That is to say with suitable conditions heat losses through the plug are zero, since the outside surface is at the temperature of the bath. Any effect on the readings of heat losses through the support of the plug was prevented by not allowing the water which passes close to the support to approach the bulb of the thermometer, which was accomplished by dividing the flow as indicated by the arrows in the figure. The effectiveness of the protection from heat losses is proved by the lack of systematic variation of the value of the mechanical equivalent with different rates of flow through the plug.

[1] PHYS. REV., 30, 529, 1910.

Early in the work it proved necessary to make the water flow similarly and spirally around the coil of each thermometer. This is probably due to small variations in the temperature at different points in the cross section of the flow, due to the fact that the center of the stream is farthest from the bath water and flows fastest. This was unexpected since stream-line motion breaks down at lesser velocities than those used in the copper tubing. Barnes[1] found the same thing in his work. Arranging the flow spirally mixes it by the swirling motion and gives an average temperature reading. Following the use of this the readings became much more consistent. The spiral was made of a small size rubber tubing held in place by a wire threaded through it and soldered at the ends to the thermometer case. It also made necessary the glass return flow tube inside the plug. The course of the water is shown by the arrows in the figure.

For solutions passing through a porous wall various observers[2] have noted a semipermeable wall effect, that is the dissolved substance is held back somewhat by the wall so that the solution escaping would have a lower concentration than that just at the wall. This mechanically forced dilution of the solution requires work. After a steady state has been reached the fluid passing both thermometers will be alike in concentration of impurities and if the passing of the fluid into and out of the more concentrated zone takes place adiabatically the resultant work required will be zero. In case the distilled water has enough impurities present to show this effect, these changes must have taken place within the filter paper layer where their resultant effect will be zero.

It has long been known that a liquid driven through a capillary in a nonconducting material results in a difference of electrical potential between the ends. In the present case the ends were short circuited by the metal parts so that any motion of charge was not against a difference of potential and hence there was no work involved.

The rate of flow through the plug was measured by reading the pressure drop between the plug and the reservoir by mercury in a U-tube. It was callibrated by reading the pressure drops for a set of rates of flow where these were determined by measuring the delivery in a definite time. No attempt was made to read the flow to better than 1 per cent. accuracy.

Thermometer Resistance Box.

The resistance box was of the regular equal-arm Wheatstone bridge type, with solder or mercury connections in heavy copper throughout.

[1] Phil. Trans. Roy. Soc., *A*, 199, 149, 1902.

[2] Cf. Bigelow and Bartell, J. Am. Chem. Soc., 31, 1194, 1909.

The coils of manganin or advance wire, silk-covered, were wound noninductively on metal spools, heavily shellacked, and held at steam temperature for days for annealing and drying. The unit of resistance was approximately ¼ ohm. One centimeter of bridge wire corresponded to 0.002 units. The ratio coils were wound noninductively and together on the same spindle, with the four terminals dipping in four mercury cups so that by lifting and rotating through a right angle the ratio coils could be reversed. Their ratio differed from unity by 1 part in 30,000 throughout the work. A mercury cup commutator was used for making the thermometer connections. A removable coil with terminals in mercury cups served to balance most of the resistance of the thermometer. Its place could be taken by a series of coils approximately equal to the box coils, whose use greatly facilitated the box callibrations. Reference must be made to Barnes's paper cited above for the general method of callibration of coils and wire. The box was provided with heating coil, stirrer, and thermostat, and the temperature held at 25° C. during use.

Box Coil Calibrations.

Date.	Nov. 23, 1910.	Dec. 15, 1910.	Feb. 21, 1911.	Mar. 13, 1911.	Sept. 9, 1911.	Nov. 7, 1911.	Feb. 6, 1912.
Coil.	1	2	3	4	5	6	7
0.0625	−0.7	−0.5	−0.2	−0.7	−0.3	−0.2	−0.8
0.125	−1.6	−1.7	−2.5	−1.7	−2.0	−1.5	−0.9
0.25	−4.8	−4.2	−3.9	−4.6	−5.3	−3.2	−3.5
0.5	1.1	0.9	0.5	1.2	−0.2	1.7	1.9
1.0	0.3	0.3	1.0	0.3	1.5	2.4	2.2
2.0	−2.6	−2.2	−2.4	−2.8	5.7	0.9	1.9
4.0	−3.7	−3.6	−3.7	−3.9	10.0	2.7	3.1
8.0	−3.0	−6.8	−7.0	−9.0	16.7	3.4	−1.1
16	−0.2	0.4	−3.9	−1.7	8.2	1.2	28.8
32	37.1	42.4	36.6	38.1	36.3	49.8	28.0
64	0.0	0.0	0.0	0.0	0.0	0.0	0.0

The corrections are box units × 10^4.

The box was callibrated at frequent intervals and it quickly developed that the resistances were changing continuously by quite serious amounts. Rosa[1] attributes this to the varying hygroscopic condition of the shellac resulting in variation in strain on the wire. As he recommends, the coils were enclosed in moisture tight containers which reduced but did not eliminate the variations. Addition of scrap metallic calcium to the bath oil as a water and acid absorbing agent did not help materially nor did omitting the shellac on some test coils. The variations now however

[1] Bull. Bur. Stand., 5, 553, 1907.

were of quite manageable size entering only into the actual temperature readings and hardly at all into the differential readings used in the work. The callibrations covering the period of the readings are given in Table I. where the numbers are the corrections in box units times 10^4.

The galvanometer was of the Broca type with all copper circuit and magnetic shielding. It was used only as a zero instrument. The sensibility was about 10^{-10} and was kept sufficiently high to allow of setting with certainty to 0.0001° C. In both callibration and use a current of about 0.01 ampere was kept flowing continuously, and readings were made by reversing the current which therefore did not vary the slight heating effect and also doubled the galvanometer reading.

THERMOMETERS.

To approach the desired accuracy in the temperature readings it was necessary to read to 0.0001° C. This made imperative the use of high resistance in the thermometers and all those used in the readings had fundamental intervals of about 25 ohms. Even with fine wire the standard mica frame became too bulky for the purpose; the most satisfactory one found and that used with the platinum thermometers, was made by cutting a double thread on a soapstone cylinder and hardening it by heating to a white heat. It was then wound so that the wire fell below the edge of the thread. The four leads were threaded into the end of the cylinder, thus supporting it, while the thermometer wire was led out through small holes and silver soldered to the heavy platinum leads. These in turn were silver soldered to the copper wire which was carried out of the brass case through a hard rubber block made tight by marine glue. Everything was repeatedly tested for insulation which was made perfect before use. The case was provided with an opening to the air through a calcium chloride tube and everything was put together dry. The platinum wire was obtained from the Cambridge Scientific Instrument Co., 5 meters of 0.1 mm. wire being used in each thermometer. They were annealed at a low red heat and callibrated at 0° C., 100° C. and 444.6° C. The ice point determinations were made in a double ice bath protected by an air space and asbestos covering. Barnes has shown, and my experience agrees with his, that the temperature of the ice bath is very distinctly a function of the rate of melting. This melting point bath was arranged for a forced circulation down through the inner central cylinder and up the outer. In case the stirring was stopped the temperature always fell a small amount. The ice in the inner compartment melted very slowly so that it appeared advisable to break the ice fine and use the inner tank unstirred except for shifting the thermom-

eters which produced usually a slight rise in the temperature followed by a fall close to the former value. The steam point was determined in the usual well protected steam bath. The pressure was read on an accurate Fortin barometer. Three groups of fundamental intervals for different thermometers are given to show the concordance obtained.

100.695	104.062	106.602
100.711	104.073	106.568
100.696	104.072	
100.706		

The complete data for the thermometers as used for the data reported farther on, is given in the following table.

THERMOMETER DATA.

	A	*B*
Resistance at 0° C.	295.93	294.09
Resistance at 100° C.	399.88	398.16
Fundamental interval	103.95	104.07
Resistance at 442.9° C.	432.90	436.07
Delta	1.748	1.567
$\frac{R_{100} - R_0}{100\ R_0}$	0.0035127	0.0035387

The sulphur point was taken as 444.6° C. The numbers are in box units, approximately ¼ ohm. The platinum used was part of a sample studied by the committee of the British Association and later taken over by the Cambridge Scientific Instrument Co. They report the delta as 1.62. The difficulty over the zero variation referred to below, led to the rewinding of the wire several times, which will probably account for the difference between the two thermometers and also for the variation in the deltas.

In work with these small temperature differences the greatest source of uncertainty of the platinum thermometers arose through the persistent and erratic shifts of zero resistance. Since the resistance was being read to less than a part in a million it was not surprising. In no case did the resistance return to the former ice point value after being at the steam temperature. That it was not due to the box coils is shown by the variation of the difference in resistance of the two thermometers both in the ice bath and in the thermostat bath. It was often of the order of thousandths of a degree. As discovered later, part but not all, was due to defective leads which changed their relative resistance when moved about, but the variations were also noted when the leads were

not disturbed. It introduced a quite uncontrollable factor into the temperature readings and was undoubtedly the cause of some of the error in the mechanical equivalent determinations.

In an effort to run down the trouble, thermometers were made of fine iron wire, silk covered, and wound on thin iron cylinders as suggested by Barnes's work with his microthermometers. Their zeros were decidedly more constant but much the same erratic variation occurred in the values of the mechanical equivalent as determined with them. These results supported the belief that the platinum thermometers were much more reliable than had been inferred from the mechanical equivalent results. Further confirmation came from the excellent agreement between the calculated and determined differential readings at a series of temperatures near 4° C.

Working Temperature.

In the theoretical discussion above, reference is made to the possibility of having a zero change of temperature on reversible adiabatic expansion between given pressure limits by a suitable choice of initial temperature. An experimental study soon to be published showed for the pressure limits 34 kg/cm^2 to 1 kg/cm^2, that the temperature was 3.59° C. Between the limits 3.53° C. and 3.65° C. the temperature change was less than 0.0001° C. and hence all of the readings were made with bath temperature lying between these limits. The similar pressure limits were 31.5 kg/cm^2 and 35.5 kg/cm^2.

Experimental Method.

The bath and the resistance box were first brought to the desired temperatures and the thermostats set working steadily. The two thermometers were placed for their full case lengths in the water of the bath with the bulb end in the inner bath and their difference of resistance read with a steady current till the readings became constant for 5 to 10 minutes. They were then put into their places in the system with as little exposure to room temperature as possible and the pump started. Throwing this sudden change of load on the thermostat upset its steady working for a few minutes but as soon as the pump and the supply tank were cooled down somewhat and reached a steady state the thermostat was back in steady working order. The speed of the pump was adjusted to give nearly the flow required after which the regulator held the pressure constant while the flow decreased somewhat due to the partial clogging of the plug by fine suspended material in the water. This clogging decreased rapidly as the water cleared of suspended particles. The pressure was then admitted very slowly to the manometer. If the water

surfaces were displaced rapidly by the mercury, the water clung in a thick layer to the glass in the capillary tubes and when the flow had ceased, the water gathered together, making small gaps in the mercury columns, which consequently had to be carefully guarded against. At the same time the pressure was applied, the air circulating fan was started. The compression of the mercury and of the water, the expansion of the glass, and the admission of cold water from the circulating system, all tended to disturb the temperature conditions so that the manometer was never read till at least half an hour after the pressure was first applied. During this time the plug conditions and the thermostat were becoming steady. As soon after this as the plug temperature difference became constant for 5–10 minutes and the manometer surfaces showed no shift for the same time, the valve to the manometer was shut down, the pump stopped, and the reading of the manometer differences of level carried out as rapidly as possible. The readings were made from the low pressure surfaces to the high pressure surfaces of the eight tubes, reading the temperature on the five case thermometers during the process, and the setting on the first tube was repeated. It sometimes showed a rise and sometimes a fall of the higher surface, never more than a millimeter either way, and was as small as could be expected considering the way the tape was carried on the sliding support and also considering the way the temperature of the water and the mercury could have varied. The manometer did not leak as shown by leaving the pressure on it for hours or a small pressure for days. At the completion of the manometer settings requiring about 25 minutes, in the later readings when experience had shown it to be advisable, the thermometers were replaced in the inner bath and the difference of their resistances again determined. In the earlier readings with the platinum thermometers this difference in their resistances was determined before or after the plug reading, and differed so markedly from day to day that a part of the variation of the results is to be attributed to this cause.

In the only group of readings considered of sufficient accuracy to report in detail the procedure was varied somewhat to avoid the necessity of comparing the thermometers at the bath temperature. A determination of the flow difference of temperature was made and the manometer read, the thermometers were then reversed in position and both readings repeated. The mechanical equivalent (C) calculated from the sum of these differences of temperature and differences of pressure eliminated the determination of the difference of resistance at the same temperature and all that was required of this difference of resistance was that it should remain constant during the pair of readings. The complete set made in this way is reported.

No.	Press. Change.	Temp. Change.	Temp.	Flow.	C	Per Cent.
1	65,808	1.5281	3.556	675	4.2081	−0.04
2	65,446	1.5187	3.570	1,425	4.2123	+0.06
3	65,572	1.5230	3.550	1,175	4.2086	−0.03
4	65,706	1.5272	3.551	1,080	4.2057	−0.10
5	65,669	1.5259	3.550	1,025	4.2069	−0.07
6	65,683	1.5279	3.550	980	4.2027	−0.17
7	65,812	1.5295	3.537	770	4.2065	−0.08
8	65,867	1.5313	3.537	650	4.2051	−0.12
9	65,871	1.5290	3.533	400	4.2127	+0.04
10	65,559	1.5196	3.571	1,240	4.2156	+0.17
11	65,460	1.5193	3.557	1,370	4.2116	+0.05
12	65,464	1.5156	3.557	1,370	4.2221	+0.29
				Average	4.2099	

In the above the pressure is expressed in kg/cm^2, the temperature in degrees centigrade, the flow in c.c./min., and C in joules/calorie in terms of the calorie at the average temperature 3.99° C. In the calculations of these readings the density of the water and of the mercury at the average temperature is taken from the tables of Landolt-Bornstein, as is also the specific volume of the water and the coefficients of compressibility. The small correction for the error of the tape was applied, but no correction for the temperature since the coefficient of expansion is so small. The value of gravity used, 980.36 cm/sec^2 was that determined by E. Smith.[1]

In the above table all the readings except the last (No. 12) were made with the same plug having a round porous end, but the flow arrangements differed slightly at different times, since it was necessary to dismount the plug to clean it and the flow guides could not be replaced in identically the same way. The rate of flow varies markedly but the value of the mechanical equivalent shows no systematic variation with it. This proves the above theory of this form of porous plug at least to the accuracy here shown. It also shows that water takes a very short time to attain its equilibrium condition after the removal of pressure which was not by any means to be confidently expected. The average of the whole set unweighted is 4.2099. The last reading was made with a plug with a metal (non-porous) end and although it was well covered there was undoubtedly some heat loss and the value of C would be too high. If this is omitted the average becomes 4.2087, while Barnes's value for this temperature is 4.2078. Barnes's method is so different from the present one, that this agreement (0. 02 per cent.) gives ground for the belief that systematic errors are fairly well eliminated and that those remaining are

[1] U. S. Coast and Geodetic Survey, Special Publication No. 12, page 9.

largely chance errors of individual readings which will average out more or less completely. On account of the unusual working temperature direct comparison with other worker's data does not seem profitable at this time.

The probable sources of uncertainty are of some interest. The regulation of both temperature and pressure left nothing to be desired. The most serious known source lay in the uncertain variation of the differential resistance of the platinum thermometers. All the experimental evidence indicates that the manometer recorded pressure to the desired accuracy, and the only further confirmation would be to test its reproducibility by means of some reliable constant pressure. The change produced by placing the flow guides around the thermometers leaves some doubt as to whether error due to irregularity of flow has been absolutely eliminated. It is the writer's belief that the data presented in this paper, while the result of several years work, is not yet as consistent as the method can be made to yield; and it is his intention to return to the work again as soon as circumstances allow.

My thanks are due to Professor Snow and to Professor Mendenhall for placing the laboratory facilities at my disposal for the work, and to Professor Mendenhall also for his very valuable criticism of the manuscript.

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UNIVERSITY OF WISCONSIN,
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A STUDY OF SOME CHANGES IN THE AIR-LIQUID CONTACT POTENTIAL DIFFERENCE.

BY G. W. MOFFITT.

IN spite of the fact that much work has been done on the investigation of contact potential differences very little can yet be said with certainty, except in the case of metals, concerning either the nature or the magnitudes of the potential differences between different substances in contact. The early investigators were handicapped by apparatus of low sensitiveness and in some cases by a preconceived and decided notion of the phenomenon under investigation. In fact, the history of the subject presents to us a long series of lengthy wordy arguments between the exponents of the electrochemical theory and those of the contact theory. Often there is little experimental foundation for the conclusions reached, direct experimental results being discordant seemingly from the very nature of the phenomenon. And yet we find instances where results are given to the fourth decimal place when the apparatus was inaccurate in the third place and the observed quantity varied in the second place.

The greater part of the time and thought of investigators in contact electricity has been directed toward the solution of the problem for metals. Nevertheless we find at an early date a few investigators who did very good work in pioneering the difficult problem of metal-liquid and liquid-liquid contact potential differences. We find that Volta, Davy, Buff, Becquerel, Pfaff, Péclet, Kohlrausch, Hankel, Gerland, Clifton, Ayrton and Perry, and others have made experiments using various inductive methods.

As early as 1807 Davy,[1] in a paper entitled "Some Chemical Effects of Electricity," describes some condenser experiments which he had made using various liquids.

In 1824 Becquerel[2] attempted the investigation of metal-liquid contact potential differences. He placed the liquid in a metal vessel which stood on the upper plate of a condenser connected to an electroscope, and connected the liquid to the condenser with his fingers. He tried merely to find the sign of the electrification.

[1] Ann. de Chim. [I.], LXIII., p. 230, 1807.
[2] Ann. de Chim. et de Phys., XXV., p. 405, 1824.

Buff[1] made the lower plate of his condenser of the metal to be examined. Above it he placed a sheet of glass and on the glass a piece of filter paper soaked in the liquid. He connected the moist filter paper to the metal plate by means of a wire of the same metal.

Kohlrausch[2] made some experiments on the difference of potential of liquids in contact. He too used filter paper wet with the liquids as his condenser plates. For this reason, as we shall see later, we cannot give much weight to his results.

Hankel[3] used a modified Kohlrausch method and investigated metal-liquid potential differences without introducting blotting paper, fingers, or glass, as the earlier experimenters had done. He employed a wide funnel connected by a tube to a small cup. The vessel was filled level full of the liquid and the metal electrode was placed in the cup. Immediately above the liquid in the funnel was a copper plate. This plate was put in metallic contact with the electrode, then insulated, lifted, and connected to a Hankel electrometer. A zinc plate was then substituted for the liquid and the experiment was repeated. The metal-liquid potential difference was then deduced in terms of the contact potential difference between zinc and copper. Air-liquid contacts were neglected throughout the work. The observed values were found to vary considerably; for instance, freshly polished copper and water gave values from 0.09 to − 0.11 Zn/Cu.

Clifton[4] used a quadrant electrometer, one pair of quadrants connected to the upper condenser plate, the other pair to the lower plate. The upper plate was of the metal under observation. On the lower plate was placed a dish of the liquid to be used and an electrode of the same metal as the upper plate dipped into the liquid and made metallic contact with the lower plate. A means of charging the quadrants and the connected condenser to any desired potential difference was supplied through a key which could also serve to bring the quadrants to the same potential.

He assumed that the surface condition of his condenser plate was a constant and made no mention of the possible existence of a potential difference at the air-liquid contact. His results are referred to Zn/Cu, which he seemed to think was more constant than a Daniell or a Clark cell. He gave it as 0.8516 volt, but it is to be noticed that separate determinations disagreed in the second decimal place. He also gives potential diagrams of various voltaic circuits. These diagrams are apt to prove misleading, however, because the magnitudes of the different

[1] Ann. d. Chem. u. Pharm., XLII., p. 5, 1842; XLV., p. 137, 1844.
[2] Pogg. Ann., LXXVI., p. 200, 1850.
[3] Pogg. Ann., CXXVI., p. 286.
[4] Proc. Roy. Soc., XXVI., p. 299, 1877.

potential differences in the circuit, to say nothing of their signs, are as yet wholly undetermined.

A most thorough and comprehensive investigation of contact potential differences with liquids was begun in 1876 by Ayrton[1] and Perry in Japan. They devised an ingenious method but the apparatus required was ponderous and cumbersome. With it they made a great many determinations of metal-metal, metal-liquid, and liquid-liquid potential differences. The principle of their method was as follows:

"Let 3 and 4 be two insulated gilt brass plates connected with the electrodes of a delicate quadrant electrometer. Let 1 under 3 and 2 under 4 be the surfaces whose contact potential is to be measured. 3 and 4 are first connected together and then insulated, but remain connected to their respective electrometer quadrants. Now 1 and 2 are made to change places with one another, 1 being now under 4 and 2 under 3, then the deflection of the electrometer will give a measure of the difference of potential between 1 and 2."

The experimental difficulties encountered in interchanging 1 and 2 and still preserving the necessary constant capacity relations, especially when one or both surfaces were liquids, will be at once realized.

In their measurements no account is taken of air-metal contacts, and air-liquid contacts were considered negligible, if they had any influence at all. Before they finished their work, however, their views underwent a change and in their last paper they clearly state that their experiments leave the question of air-liquid contacts undecided. If 1 and 2 were two liquids, L_1 and L_2, what they really measured was

$$L_1L_2 + L_2 \text{ air} - L_1 \text{ air},$$

that is, the liquid-liquid contact potential difference plus the difference of the two air-liquid contact potential differences. They placed great confidence in the constancy of the contact potential difference between zinc and copper which they used as a standard at 0.75 volt (Clifton gave it as 0.8516 volt). And they agreed with Clifton that it was more constant than a Daniell or a Clark cell, although Pellat found it to vary as much as three tenths of a volt. They have tabulated the results of numerous observations which on examination reveal discrepancies many times larger than the limit of sensibility of their apparatus.

Turning to electrochemistry we have the solution pressure theory of electrode potentials and of diffusion potential differences developed by Nernst, Ostwald and others. For dilute solutions of electrode salts theory agrees fairly well with experimental results on concentration cells.

[1] Phil. Trans., Part I., 1880.

For measurements of single potential differences the electrochemists depend on the Lippmann electrometer and the dropping mercury electrode, which are based on the Helmholtz theory of the electric double layer. These are familiar to most physicists and it is not the writer's intention to review the numerous researches in this field of electrochemistry. There are, however, a few papers that may well be noticed here. Billitzer[1] has shown that the maximum surface tension for mercury in contact with a liquid does not necessarily occur when there is no difference of potential between the metal and the liquid. He showed by several methods that it may vary as much as several tenths of a volt, and he came to the conclusion that methods of measuring metal-liquid contact potential differences depending on the Helmholtz theory of the electric double layer are inaccurate. Krouchkoll[2] found similar results with wires under tension as electrodes. These results were also confirmed by Exner and Tuma, and also by Brown.[3]

Summing it all up, we may say that no experimental determination that is entirely free from objection has as yet been made of any electrode potential, or of any liquid-liquid potential difference, and that the question of the air-liquid contact potential difference has merely been raised.

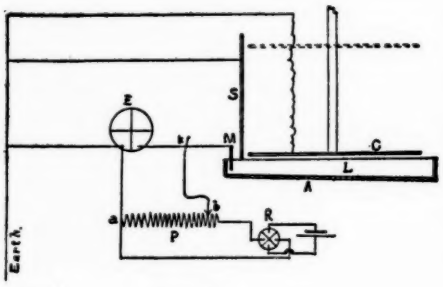


Fig. 1.

The purpose of this investigation was to devise a simple and satisfactory method for the study of contact differences of potential in those cases where liquids enter into consideration, and to seek out and eliminate if possible the unknown sources of erratic error which have caused such discrepancy in the experimental results of previous investigators. As is usually the case, the whole aim of the work has not been realized, but enough has been done to show that the problem of contact potential differences with liquids is more complex than has been thought. Factors heretofore neglected will be shown to play an important part, at least at the air-liquid contact.

A form of the compensation method was used. Fig. 1 is a diagram of the electrical connections. *A* is an insulated glass vessel 24 centimeters in diameter and less than a centimeter in depth, in which is placed the

[1] Zeitschr. Electrochem., 14, p. 624, 1908.
[2] Ann. chem. phys. [VI.], 17, p. 129, 1889.
[3] Phil. Mag. [V.], 17, p. 384, 1889.

liquid (L) under observation. C is a lacquered brass plate 20 centimeters in diameter, which, in its lowest position, stands a few millimeters above the surface of the liquid. It is arranged so that it may be easily raised to a height of 6 or 8 centimeters above the liquid while the observer is watching the electrometer scale. This plate is connected permanently to earth. M is a small electrode of the metal under observation. It is supported on an insulating stand entirely separate from the glass vessel and it is connected permanently, during an experiment, to he insulated quadrants of a Dolazalek electrometer, by means of a mercury cup and a brass wire. The other pair of quadrants is permanently connected to earth. S is an earthed electrode screen that prevents any inductive effect on the electrode by the motion of the plate C. P is a Wolff potentiometer by means of which the insulated quadrants and the electrode are brought to any desired potential through the key k, which also serves as the earthing key. R is a reversing key in the main circuit of the potentiometer which permits either positive or negative potential to be applied to the electrode. The entire apparatus, except the main potentiometer circuit and the galvanometer, is protected by earthed screens.

In some of the later experiments metal cell vessels were used instead of the glass vessel. One of these was plated with tin, the other with copper, so that various solutions might be used without chemical action on the containing vessel. When the metal vessels were used they were not filled level full, as was the glass vessel, and to prevent error due to induction between the condenser plate and the vessel rim a cylindrical guard ring of lacquered brass was used as shown in Fig. 2. This guard ring was also used in place of the electrode screen in the later experiments using the glass vessel.

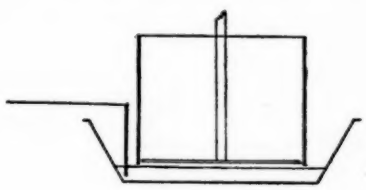


Fig. 2.

In making a reading the vessel was carefully cleaned, placed in position, and filled with the liquid to be investigated. The electrode was then rubbed bright with sandpaper, cleaned with dry filter paper, and placed in position. The condenser plate was placed at the bottom of its range of motion, and a little time allowed for the electrode potential to become steady. The potentiometer circuit was closed and the dials adjusted to any desired potential drop along ab. Then the key k was opened. On raising the plate C there was, in general, a rush of electricity to or from the electrometer. But if the *surface* of the plate and the *surface* of the

liquid were at the same potential no redistribution of charge would take place and no *change* of the electrometer reading would be observed. The potentiometer reading would be the value sought. The electrode was then removed, wiped with clean filter paper, replaced, and after a short time, the reading was checked.

It will be seen that all the advantages of a null method are retained, the electrometer acting merely as an indicator. The sensitiveness of the apparatus depends not only upon the electrometer, but also upon the ratio of the electrometer capacity to the cell capacity, and with the apparatus used it was possible to determine the balanced point within 0.002 volt. This was sufficiently sensitive for the work.

Before readings of any value could be made it was necessary to obtain a plate C whose surface potential would remain nearly constant. Pfaff and others have found that for dry or moist air and other gases, the surface potential of lacquered plates is not affected as long as there is no visible chemical action. Although used a few millimeters above the surface of liquids the plate gave no trouble. During eleven days the observed values for a copper electrode in glycerine did not vary by 0.01 volt. Copper-glycerine was occasionally used as a check on the constancy of the plate surface.

From Fig. 1 it is easily seen that what is experimentally determined is

$$K + aL + LM = E, \tag{1}$$

where K is the constant potential difference between the plate and the air, aL the potential difference between the air and the liquid, and LM that between the liquid and the electrode. If two liquids be used in succession with the same electrode we have

$$K + aL_1 + L_1M = E_1, \tag{2}$$

$$K + aL_2 + L_2M = E_2. \tag{3}$$

If a diffusion cell be set up using the two liquids we measure

$$ML_1 + L_1L_2 + L_2M = V. \tag{4}$$

Combining these three equations we have

$$L_1L_2 + L_2a - L_1a = V + E_1 - E_2. \tag{5}$$

This is in fact, what Ayrton and Perry measured, considering L_2a and L_1a negligible. With their apparatus air-liquid contacts could not be studied separately.

Consider again the observation equation

$$K + aL + LM = E.$$

The value of K may by reason of occasionally repeated check determinations, be assumed constant, although we have no means of knowing its actual magnitude. For a given liquid it is hardly possible that LM varies from time to time, and at any rate it is subject to experimental determination. We are in a position to find out whether La is a variable depending on surface condition of the liquid, gas content, and so on, and thus show its existence. And since the influence of the negative radical on the electrode potential is known to be small by reason of electrochemical data, LM will not vary much for different electrode salts. The influence of the negative radical on the air-liquid contact may then be studied.

A number of solutions of copper sulphate of different concentrations were made up. A copper electrode was used and E determined for the different concentrations. The results are plotted in Fig. 3, Curve I. This curve shows the variation of $aL + LM$ with concentration of the solution, but it does not give actual values since all readings are affected by the constant K. The same solutions were used two weeks later and Curve II. shows the results. Later on fresh solutions were made up and used with the results shown by Curve III. With zinc and zinc sulphate solutions the results were even more erratic as is shown by Curves IV. and V., which are for two sets of solutions.

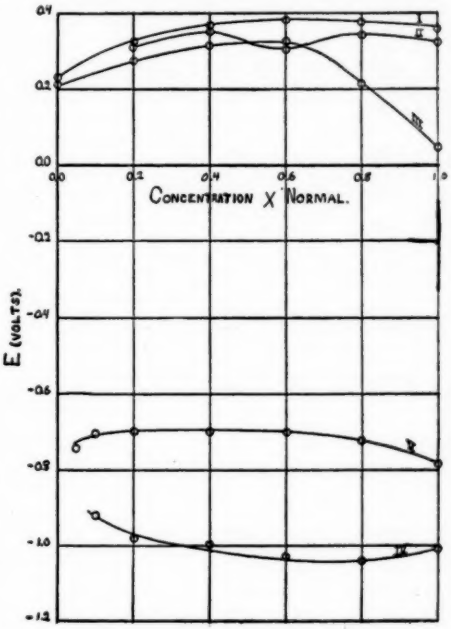


Fig. 3.

As long as results vary in this erratic way it is useless to measure the E.M.F. of the various concentration cells needed to compute $L_1L_2 + L_2a - L_1a$ for different concentrations of the same solution, and to tabulate results.

If these erratic values were due to a change in the value of K from day to day the result would be to add a constant to all the observed values, and the form of the curve would not be changed. Irregular variations of K large enough and rapid enough to account for the discrepancies seem very improbable. It is also improbable that LM can differ much for two solutions of the same salt at the same concentration. Neither is it

conceivable how LM for the same solution could change so much in a few days when the solution was kept in a clean glass-stoppered flask. The most probable place for differences to occur seemed to be at the air-liquid contact, and experiments were then performed to determine this point.

It was thought that the gas content of the solution might affect the air-liquid contact potential difference and with this in mind the following experiments were performed. The time of observation is recorded merely to show that the readings were made rapidly enough to eliminate the possibility of any disturbing variation of K. The experiments given are only a few of those performed with the same general results.

Copper Electrode. Normal Sodium Chloride Solution. Tinned Cell Vessel without Guard-Ring.

Liquid Surface Condition.	E (Volts).	Time.
Solution placed in cell	−0.01	3:45
Air bubbled into the solution	−0.11	4:00
Solution poured into beaker and at once poured into cell	−0.02+	4:18
	−0.03	4:30
Air bubbled in place	−0.13	4:35
	−0.13	4:50
Air bubbled again	−0.14	5:00
Poured into beaker and at once returned to cell	−0.04	5:10
Air bubbled in place	−0.12	5:15

Copper Electrode. Normal Sodium Chloride Solution. Tinned Cell Vessel with Guard-Ring.

Liquid Surface Condition.	E (Volts).	Time.
Solution placed in cell	−0.11	9:00
Air bubbled in place	−0.16+	9:10
Air bubbled again	−0.17	9:20
Poured into beaker. At once returned to cell	−0.05+	9:30
Air bubbled in place	−0.16	9:45
Swept with clean filter	−0.23	9:50
Poured into beaker and at once returned to cell	−0.09	10:00
Swept with clean filter	−0.24	10:10

From the first experiment it is evident that the variation in the air-liquid contact potential difference is not wholly due to dissolved gases since pouring the solution out of the cell and at once returning it returns the reading to its first value. The change due to air bubbling is practically the same in each case, and causes a shift toward negative values. In the second experiment the guard-ring was used and actual values are different, but the same general effect due to pouring and to air bubbling is noticed. Sweeping with filter paper produces an effect

much greater than that produced by air bubbling and in the same direction.

In the following trial with a 0.4 normal copper sulphate solution in the copper-plated vessel using a copper electrode, the liquid surface was repeatedly swept until a steady value was obtained.

Liquid Surface Condition.	*E* (Volts).	Time.
Solution placed in cell	+0.31−	1:55
Swept with clean filter	+0.21	2:00
Poured into beaker and at once returned to cell	+0.27	2:07
Swept with filter paper	+0.17−	2:13
Air bubbled in place	+0.13	2:25
Swept with clean filter	+0.06	2:30
Air bubbled in place	+0.06	2:40
Swept with clean filter	+0.03	2:43
Again swept with filter	+0.01	2:46
Again swept with filter	−0.00+	2:50
Again swept with filter	−0.02	2:55
Again swept with filter	−0.03−	3:00
Poured into beaker and at once returned to cell	+0.11	3:06
Again poured into beaker and returned to cell	+0.20	3:15
Again poured into beaker and returned to cell	+0.22	3:25
Again poured into beaker and returned to cell	+0.24	3:30
Drop of kerosene on surface	0.00	3:37
Another drop added	−0.02−	3:41
Poured into beaker, vessel cleaned, solution returned	+0.02	4:25
A drop of kerosene added	−0.02	4:30
About 1 c.c. kerosene added	−0.01	4:35

It is seen that a limiting low value was approached as the surface was repeatedly swept with filter paper. It is also of interest to note that a few drops of kerosene instantly produced the same effect as did continued sweeping with filter paper, and the addition of considerable kerosene produced the same change as did a very thin film of it.

The effect of drawing a clean glass rod reaching clear across the vessel, over the surface thus securing a clean surface, was then tried. In order to do this the glass vessel was used level full of the liquid. The copper electrode and the 0.4 normal copper sulphate solution was used with the following results.

Liquid Surface Condition.	E (Volts).	Time.
Poured into vessel	+0.17−	10:00
Swept with clean filter	+0.12	10:08
Again swept with filter	+0.10	10:11
Swept with clean glass rod	+0.29	10:20
Swept with filter paper	+0.21−	10:30
Swept with clean glass rod	+0.36	10:36
Again swept with rod	+0.39	10:44
Again swept with rod	+0.42	10:49
Again swept with rod	+0.43	10:52
Again swept with rod	+0.43+	10:55
Swept with clean filter	+0.29	11:00
Again swept with filter	+0.19	11:02
Again swept with filter	+0.14	11:06
Small drop kerosene added	+0.10	11:08
Another drop kerosene added	+0.09	11:12
Swept with clean glass rod	+0.14	11:16

In every case sweeping with the glass rod raised the value toward a maximum limit, and continued sweeping with filter paper reduced the value toward a lower limit.

A normal sodium chloride solution was next tried with the copper electrode, and the effects of alcohol and ether vapor and kerosene are shown below.

Liquid Surface Condition.	E (Volts).	Time.
Swept several times with glass rod	+0.05	9:15
Again swept with glass rod	+0.06	9:22
Undisturbed	+0.06−	9:36
Three drops alcohol put on. Negative at first but before a reading could be made was	+0.03	9:44
Three more drops alcohol, first reading	0.00	9:49
	0.00	10:12
Ether vapor poured on	−0.10	10:15
Undisturbed	−0.03	10:28
Undisturbed	−0.05	10:39
Drop kerosene put on	−0.18	10:46
Another drop kerosene put on	−0.21+	10:50
Another drop kerosene put on	−0.22	10:52
Another drop kerosene put on	−0.22−	10:55

Besides showing the effects produced by various substances this experiment shows three separate determinations with distilled water agreeing well among themselves. In all the cases tried the difference between the high clean surface value and the low filter swept or kerosene surface was found to be about 0.3 volt.

Copper Electrode with Distilled Water using Glass Vessel with Electrode Screen.

Liquid Surface Condition.	E (Volts).	Time.
Swept several times with glass rod	+0.29	9:30
Again swept with rod	+0.29	9:34
Again swept with rod	+0.29−	9:36
Screen replaced by guard ring	+0.29	9:48
Vessel emptied. Refilled. Swept with glass rod	+0.28	9:55
Swept some more with rod	+0.27+	
Some cork dust sprinkled on	+0.26	10:00
Drop of kerosene. Cork dust swept to edge of vessel	+0.01	10:06
Another drop of kerosene	−0.03−	10:10
Another drop of kerosene	−0.03−	
Cell emptied, cleaned and refilled. Swept with rod	+0.28+	10:24
Drop toluene added. A decrease but before a reading could be made it was	+0.27	10:39
More toluene added	+0.25	10:42
Drop cotton-seed oil added	+0.04	10:55
Several drops more	+0.04	10:57
Drop of kerosene added	+0.04+	10:59
Several drops more	+0.03−	11:02
Cell emptied. Refilled without cleaning. Some oil still on the surface	+0.03	11:20
Swept[1] several times with rod	0.00	11:30
Swept[1] several times with rod	−0.04	11:35
Swept[1] several times with rod	−0.05	11:41

Since the air-liquid contact potential difference has thus been varied as much as three tenths of a volt its general existence cannot be denied. In what special cases it may be zero or negligibly small we do not know Neither do we know its magnitude nor its sign in any case, but we see from the above experiments that the clean liquid surfaces used are more positive to air than are the contaminated surfaces.

Experiments were next made to find the variation of E with the concentration of the solution, taking in each determination the final value for a clean liquid surface. The copper electrode was used in all these experiments.

NaCl (Normal Solution).

Swept with glass rod	−0.05
Swept some more	−0.02
Swept some more	0.00
Swept some more	+0.01−
Swept some more	+0.01−

NaCl (0.4 Normal).

Swept as before	−0.03
Swept some more	+0.05
Swept some more	+0.04
Swept some more	+0.05

[1] The sweeping removed the small globules of cottonseed oil leaving a film of kerosene.

NaCl (0.2 Normal).

Swept as before	+0.08
Swept some more	+0.11−
Swept some more	+0.10−
Swept some more	+0.10
Swept some more	+0.10

Water (Distilled).

Swept as before	+0.28
Swept some more	+0.28

This gives clean liquid values for E as follows:

Water	+0.28
NaCl (0.2 normal)	+0.10
NaCl (0.4 normal)	+0.05
NaCl (normal)	+0.01−

Solutions of copper sulphate, copper chloride, sodium chloride, bromide, and sulphate were used in the same way. The results in volts are tabulated below and curves are plotted in Fig. 4.

Curve.	Conc. →	∞	0.15	0.20	0.25	0.30
A	NaCl	+0.28		+0.10		
B	$CuSO_4$	+0.28+		+0.30		
C	$CuCl_2$	+0.28+			+0.33−	
D	$CuCl_2$	+0.28			+0.32	
E	NaCl	+0.29	+0.10			+0.07
F	Na_2SO_4	+0.29	+0.22−			+0.20−
G	NaBr	+0.28	+0.06			+0.03
H	$CuSO_4$	+0.28+	+0.35			+0.37−

Curve.	Conc. →	0.40	0.50	0.60	1.00
A	NaCl	+0.05			+0.01−
B	$CuSO_4$	+0.31−			+0.31−
C	$CuCl_2$		+0.33		+0.30
D	$CuCl_2$		+0.33+		+0.30
E	NaCl			+0.05+	+0.04−
F	Na_2SO_4			+0.19−	+0.19
G	NaBr			+0.00+	−0.02+
H	$CuSO_4$			+0.36	+0.36−

A and *E* were made with entirely different solutions, as were also *B* and *H*. *C* and *D* were made with solutions diluted from the same stock solution, but otherwise they are entirely separate. The two curves differ at no point by a hundredth of a volt. *F* and *G* were not repeated.

We see in these results much better duplication of readings than was possible before, but the discrepancies are still quite large and it does not yet seem advisable to compute and tabulate values of $L_1L_2 + L_2a$

$-L_1a$. To do so before the causes of the discrepancies are better understood would be to add to an already confusing mass of more or less conjectural data of doubtful value.

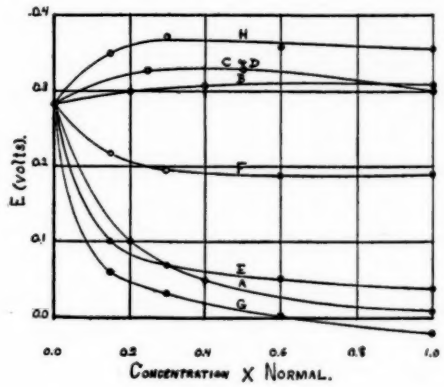


Fig. 4.

The following concentration cells were set up and the electromotive force measured with the potentiometer.

Cu-Na_2SO_4 (n)–NaCl (n)-Cu	0.164 volt.
Cu-$CuCl_2$ (n)–$CuSO_4$ (n)-Cu	0.004
Cu-$CuSO_4$ (n)–NaCl (n)-Cu	0.27
Cu-$CuSO_4$ (n)–NaBr (n)-Cu	0.35
Cu-Na_2SO_4 (n)–NaBr (n)-Cu	0.208

Combining these with the values of E taken from the curves we have the following table.

The Following Has	To the Following	A Contact P.D. in Volts.
$Na_2SO_4(n)$	NaCl(n)	$\begin{cases} +0.01 \\ -0.02 \end{cases}$
$CuSO_4(n)$	$CuCl_2(n)$	−0.01
$CuSO_4(n)$	NaCl(n)	$\begin{cases} -0.03 \\ 0.00 \end{cases}$
$CuSO_4(n)$	NaBr(n)	+0.02
$Na_2SO_4(n)$	NaBr(n)	0.00

These results are the differences of the two air-liquid contact potential differences plus the diffusion potential between the two solutions. This last, according to the electrochemists, is small for the solutions used. Then it would seem that the air-liquid contact potential differences for normal solutions with clean surfaces has approximately the same value for the solutions examined.

It was pointed out by Ayrton and Perry that if their experiments were performed in gases other than air the question of air-liquid contact potential differences could be solved. Their apparatus would have given differential results, however, and would have left the question of gas-liquid contact potential differences unanswered. With the writer's apparatus this problem may be more easily attacked, and if the surface potential of the condenser plate does not change when immersed in different gases, the difference of the gas-liquid potential difference for different gases may be directly observed.

At best experimental work in this field is tedious. Slight impurities in the water used in making the solutions seem to have considerable effect especially with solutions of low concentration. Distilled water of the best quality and in quantity sufficient for work of this kind could not be had, and it is possible that the discrepancies still in evidence may be traceable to this cause. It is the writer's intention to so modify the apparatus that a much smaller quantity of solution will suffice, and to investigate further the questions that have arisen.

The writer's thanks are due to Professors Sanford and Rogers for their kindly suggestions and criticism during the progress of the work.

SUMMARY.

1. Contact potential differences with liquids have been studied by means of the inductive method.

2. The general existence of a potential difference at the air-liquid contact has been definitely shown.

3. The air-liquid contact potential difference may vary as much as three tenths of a volt, depending on the condition of the liquid surface.

4. Water and the aqueous solutions used are more positive to the air when the surface is clean than when it is contaminated.

5. The value of the air-liquid contact potential difference (for the solutions studied) is approximately the same for aqueous solutions of different salts at normal concentration.

STANFORD UNIVERSITY,
April, 1913.

ON THE ELEMENTARY ELECTRICAL CHARGE AND THE AVOGADRO CONSTANT.

By R. A. Millikan.

1. Introductory.

THE experiments herewith reported were undertaken with the view of introducing certain improvements into the oil-drop method[1] of determining e and N and thus obtaining a higher accuracy than had before been possible in the evaluation of these most fundamental constants.

In the original observations by this method such excellent agreement was found between the values of e derived from different measurements (l. c., p. 384) that it was evident that if appreciable errors existed they must be looked for in the constant factors entering into the final formula rather than in inaccuracies in the readings or irregularities in the behavior of the drops. Accordingly a systematic redetermination of all these constants was begun some three years ago. The relative importance of the various factors may be seen from the following review.

As is now well known the oil-drop method rested originally upon the assumption of Stokes's law and gave the charge e on a given drop through the equation

$$e_n = \frac{4}{3}\pi\left(\frac{9\eta}{2}\right)^{\frac{3}{2}}\left(\frac{1}{g(\sigma-\rho)}\right)^{\frac{1}{2}}\frac{(v_1+v_2)v_1^{\frac{1}{2}}}{F}, \qquad (1)$$

in which η is the coefficient of viscosity of air, σ the density of the oil, ρ that of the air, v_1 the speed of descent of the drop under gravity and v_2 its speed of ascent under the influence of an electric field of strength F.

The essential feature of the method consisted in repeatedly changing the charge on a given drop by the capture of ions from the air and in thus obtaining a series of charges with each drop. These charges showed a very exact multiple relationship under all circumstances—a fact which demonstrated very directly the atomic structure of the electric charge. If Stokes's law were correct the greatest common divisor of this series of charges should have been the absolute value of the elementary electrical charge. But the fact that this greatest common divisor failed to come out a constant when drops of different sizes were used showed that Stokes's

[1] R. A. Millikan, Phys. Rev., 32, pp. 349–397, 1911.

law breaks down when the diameter of a drop begins to approach the order of magnitude of the mean free path of a gas molecule. Consequently the following corrected form of Stokes's law for the speed of a drop falling under gravity was suggested.

$$v_1 = \frac{2}{9}\frac{ga^2(\sigma - \rho)}{\eta}\left\{1 + A\frac{l}{a}\right\}, \tag{2}$$

in which a is the radius of the drop, l the mean free path of a gas molecule and A an undetermined constant. It is to be particularly emphasized that the term in the brackets was expressly set up merely as a first order correction term in l/a *and involved no theoretical assumptions of any sort;* further that *the constant A was empirically determined* through the use only of small values of l/a and that *the values of e and N obtained were therefore precisely as trustworthy as were the observations themselves.* This fact has been repeatedly overlooked in criticisms of the results of the oil-drop method.[1]

Calling then e_1 the greatest common divisor of all the various values of e_n found in a series of observations on a given drop there resulted from the combination of (1) and (2) the equation

$$e\left(1 + A\frac{l}{a}\right)^{\frac{3}{2}} = e_1, \tag{3}$$

or

[1] Indeed M. Jules Roux (Compt. Rendu, 152, p. 1168, May, 1911) has attempted to correct my values of e and N by reducing some observations like mine which he made on droplets of sulphur, with the aid of a purely theoretical value of A which is actually approximately twice too large. The impossibility of the value of A which he assumes he would himself have discovered had he made observations on spheres of different sizes or at different pressures. Such observations whether made on solid spheres or on liquid spheres always yield a value of A about half of that assumed by Roux. Hence his value of e, viz., $e = 4.17 \times 10^{-10}$ rests on no sort of experimental foundation whatsoever. It rests rather on two erroneous assumptions, first the assumption of the correctness of the constants in Cunningham's theoretical equation (Proc. Roy. Soc., 83, p. 357; see also footnote 3, p. 380, PHYS. REV., Vol. 32)—constants which I shall presently show are in no case correct within the limits of experimental error even when inelastic impact is assumed, and second, the assumption that molecules make elastic impact against solid surfaces, an assumption which is completely incorrect as I had already proved by showing that the value of the "slip" term is the same for oil and air as for glass and air (PHYS. REV., Vol. 32, p. 382), which Knudsen also had proved experimentally to be erroneous (Knudsen, An. der Phys., 28, p. 75, 1909, and 35, p. 389) and which for theoretical reasons as well is plainly inadmissible, since were it correct Poiseuille's law could not hold for gases under any circumstances.

But even if Roux had assumed the correct value of A he would still have obtained results several per cent. too low, a fact which must be ascribed either to faulty experimental arrangements or to imperfect knowledge of the density of his sulphur spheres; *for solid spheres have been very carefully studied in the Ryerson Laboratory and are in fact found to yield results very close to those obtained with oil drops.* Solid spheres however are not nearly so well adapted to a precision measurement of e as are oil drops, since their density and sphericity are always matters of some uncertainty.

$$e = \frac{e_1}{\left(1 + A\frac{l}{a}\right)^{\frac{3}{2}}}. \tag{4}$$

It was from this equation that e was obtained after A had been found by a graphical method which will be more fully considered presently.

The factors then which enter into the determination of e are: (1) The density factor, $\sigma - \rho$; (2) the electric field strength, F; (3) the viscosity of air, η; (4) the speeds, v_1 and v_2; (5) the drop radius, a; (6) the correction term constant, A.

Concerning the first two of these factors little need be said unless a question be raised as to whether the density of such minute oil drops might not be a function of the radius. Such a question is conclusively answered in the negative both by theory[1] and by the experiments reported in this paper.

Liquid rather than solid spheres were originally chosen because of the far greater certainty with which their density and sphericity could be known. Nevertheless I originally used liquids of widely different viscosities (light oil, glycerine, mercury) and obtained the same results with them all within the limits of error, thus showing experimentally that so far as this work was concerned, the drops all acted like rigid spheres. More complete proof of this conclusion is furnished both by the following observations and by other careful work on solid spheres soon to be reported in detail by Mr. J. Y. Lee.

The material used for the drops in the following experiments was the highest grade of clock-oil, the density of which, at 23° C., the temperature

[1] The pressure p_2 within an oil drop is given by

$$p_2 = k + \frac{\alpha}{2R}$$

where k is LaPlace's constant of internal pressure, α the constant of surface tension and R the radius. The difference $(p_2 - p_1)$ between the pressure within the oil drop and within the oil in bulk is then $\alpha/2R$. But the coefficient of compressibility of a liquid is defined by

$$\beta = \frac{v_2 - v_1}{v_1(p_2 - p_1)}.$$

Now β for oil of this sort never exceeds 70×10^{-6} megadynes per sq. cm. (see Landolt and Bornstein's tables), while α is about 35 dyne cm. R for the smallest drop used (Table XX.) is .00005 cm.; we have then

$$\frac{v_2 - v_1}{v_1} = \beta\frac{\alpha}{2R} = \frac{70 \times 10^{-12} \times 35}{.0001} = .000024.$$

The density of the smallest drop used is then 2 parts in 100,000 greater than that of the oil in bulk. The small drops could then only be appreciably denser than the larger ones if the oil were inhomogeneous and if the atomizing process selected the heavier constituents for the small drops. Such an assumption is negatived by the experimental results given in § 9.

at which the experiments were carried out, was found in two determinations made four months apart, to be .9199 with an error of not more than one part in 10,000.

The electric fields were produced by a 5,300-volt storage battery, the P.D. of which dropped on an average 5 or 10 volts during an observation of an hour's duration. The potential readings were taken, just before and just after a set of observations on a given drop, by dividing the bank into 6 parts and reading the P.D. of each part with a 900-volt Kelvin and White electrostatic voltmeter which showed remarkable constancy and could be read easily, in this part of the scale, with an accuracy of about 1 part in 2,000. This instrument was calibrated by comparison with a 750-volt Weston Laboratory Standard Voltmeter certified correct to 1/10 per cent. and actually found to have this accuracy by comparison with an instrument standardized at the Bureau of Standards in Washington. The readings of P.D. should therefore in no case contain an error of more than 1 part in 1,000. As a matter of fact 5,000 volt readings made with the aid of two different calibration curves of the K. & W. instrument made two years apart never differed by more than 1 or 2 parts in 5,000.

The value of F involves in addition to P.D. the distance between the plates, which was as before 16 mm. and correct to about .01 mm. (l. c., p. 351). Nothing more need be said concerning the first two of the above-mentioned factors. The last four however need especial consideration.

2. The Coefficient of Viscosity of Air.

This factor certainly introduces as large an element of uncertainty as inheres anywhere in the oil-drop method. Since it appears in equation (1) in the 3/2 power an uncertainty of 0.5 per cent. in η means an uncertainty of 0.75 per cent. in e. It was therefore of the utmost importance that η be determined with all possible accuracy. Accordingly two new determinations were begun three years ago in the Ryerson Laboratory, one by Mr. Lachlan Gilchrist and one by Mr. I. M. Rapp. Mr. Gilchrist, whose work has already been published,[1] used a constant deflection method (with concentric cylinders), which it was estimated (l. c., p. 386) ought to reduce the uncertainty in η to 1 or 2 tenths of a per cent. The results have justified this estimate. Mr. Rapp used a form of the capillary tube method which it was thought was better adapted to an *absolute evaluation of* η than have been the capillary tube arrangements which have been commonly used heretofore.[2] Since Mr.

[1] Lachlan Gilchrist, PHYS. REV., 2d Ser., Vol. 1, p. 124.

[2] This investigation will shortly be published in full (PHYS. REV., 1913), hence only a bare statement will here be made of the results which are needed for the problem in hand.

Gilchrist completed his work at the University of Toronto, Canada, and Mr. Rapp made his computations and final reductions at Ursinus College, Pa., neither observer had any knowledge of the results obtained by the other. The two results agree within 1 part in 600. Mr. Rapp estimates his maximum uncertainty at 0.1 per cent., Mr. Gilchrist at 0.2 per cent. Mr. Rapp's work was done at 26° C. and gave $\eta_{26} = .00018375$. When this is reduced to 23° C., the temperature used in the following work, by means of formula (5)—a formula[1] which certainly can introduce no appreciable error for the range of temperature here used,—viz.,

$$\eta_t = 0.00018240 - 0.000000493(23 - t); \qquad (5)$$

there results

$$\eta_{23} = .00018227.$$

Mr. Gilchrist's work was done at 20.2° C. and gave $\eta_{20.2} = .0001812$. When this is reduced to 23° C. it yields

$$\eta_{23} = .00018257.$$

When this new work, by totally dissimilar methods, is compared with the best existing determinations by still other methods the agreement is exceedingly striking. Thus in 1905, Hogg[2] made at Harvard very careful observations on the damping of oscillating cylinders and obtained in three experiments at atmospheric pressure $\eta_{23} = 0.0001825$, $\eta_{15.6} = 0.0001790$ and $\eta_{18.6} = 0.0001795$. These last two reduced to 23° C., as above, are 0.0001826 and 0.0001817 respectively and the mean value of the three determinations is

$$\eta_{23} = 0.00018227.$$

Tomlinson's classical determination,[3] by far the most reliable of the nineteenth century, yielded when the damping was due primarily to "push" $\eta_{12.65° C.} = 0.00017746$; when it was due wholly to "drag" $\eta_{11.79° C} = 0.00017711$. These values reduced to 15° C., as above, are respectively 0.00017862 and 0.00017867. Hence we may take Tomlinson's direct determination as $\eta_{15} = 0.00017864$. This reduced to 23° C. by Tomlinson's own temperature formula (Holman's) yields $\eta_{23} = 0.00018242$. By the above formula it yields $\eta_{23} = 0.00018256$.

Grindley and Gibson using the tube method on so large a scale[4] (tube 1/8 inch in diameter and 108 feet long) as to largely eliminate the most

[1] See R. A. Millikan, Annalen der Physik, 1913, for a more extended discussion of this and other viscosity formulæ and measurements.

[2] J. L. Hogg, Proc. Amer. Acad., 40, 18, p. 611, 1905.

[3] Tomlinson, Phil. Trans., 177, p. 767, 1886.

[4] Grindley and Gibson, Proc. Roy. Soc., 80, p. 114, 1908.

fruitful sources of error in this method, namely, the smallness and ununiformity of the bore, obtained at room temperature the following results:[1] $\eta_{25.28^\circ C.} = .00018347$, $\eta_{23.55^\circ C.} = .00018241$, $\eta_{12.18^\circ C.} = .00018257$, and $\eta_{15.4^\circ C.} = .0001782$. These numbers, reduced to 23° C. as above, are respectively 18,245, 18,241, 18,201, and 18,195. The mean is 18,220. Grindley and Gibson's own formula, $\eta = .0001702\ \{1 + .00329t - .0000070t^2\}$, yields $\eta_{23} = .00018245$. We may take then Grindley and Gibson's direct determination as the mean of these two values, viz.: $\eta_{23} = .00018232$.

Collecting then the five most careful determinations of the viscosity of air which so far as I am able to discover have ever been made we obtain the following table.

TABLE I.

Air $\eta_{23} = .00018227$—Rapp. Capillary tube method. 1913.
Air $\eta_{23} = .00018257$—Gilchrist. Constant deflection method. 1913.
Air $\eta_{23} = .00018227$—Hogg. Damping of oscillating cylinder method. 1905.
Air $\eta_{23} = .00018258$—Tomlinson. Damping of pendular vibrations method. 1886.
Air $\eta_{23} = .00018232$—Grindley and Gibson. Flow through large pipe method. 1908.
Mean = **.00018240**

It will be seen, then, that every one of the five different methods which have been used for the absolute determination of η leads to a value which differs by less than 1 part in 1,000 from the above mean value $\eta_{23} = .00018240$. It is surely legitimate then to conclude that the absolute value of η for air is now known with an uncertainty of somewhat less than 1 part in 1,000.[2]

[1] These numbers represent the reduction to absolute C.G.S. units of all the observations which Grindley and Gibson made between 50° F. and 80° F.

[2] In obtaining the above mean I have chosen what, after careful study, I have considered to be the best determination by each of the five distinct methods. The transpiration method has been much more commonly used than have the others, and in general, the final result is in good agreement with other careful work by this method. Thus Rankine's final value (Proc. Roy. Soc., *A*, 83, p. 522, 1910) by a new modification of the capillary tube method, while probably not claiming an accuracy of more than .4 per cent., is, at 10.6° C., .0001767, a value which reduces to $\eta_{23} = .0001828$. Again Fisher's final formula (PHYS. REV., 28, p. 104, 1909) gives $\eta_{23} = .00018218$. Also Holman's much used formula (Phil. Mag., 21, p. 199, 1886, and Tomlinson, Phil. Trans., Vol. 177, part 2, p. 767, 1886) yields $\eta_{23} = .00018237$. In fact the only reliable work on η which I am able to find which is out of line with the value $\eta_{23} = .00018240$ is that by Breiterbach at Leipzig (Ann. der Phys., 5, p. 166, 1901) and that by Schultze (Ann. der Phys., 5, p. 157, 1901) and several other observers at the University of Halle who used Schultze's apparatus (Markowski, Ann. der Phys., 14, p. 742, 1904, and Tanzler, Verh. der D. Phys. Ges., 8, p. 222, 1906). None of these observers however were aiming at an absolute determination, but rather at the effects of temperature and the mixing of gases upon viscosity and their capillaries were too small (of the order .007 cm.) to make possible an absolute determination of high accuracy. Their agreement among themselves upon a value which is about 1.3 per cent. too high is partly accounted for by the fact that everal of them used the same tube. None of the m made any effort to eliminate the necessarily large error in the measurement of so small a bore (which appears in the result in the fourth power) by taking the mean of η from a considerable number of tubes.

A second question which might be raised in connection with η is as to whether the medium offers precisely the same resistance to the motion through it of a heavily charged drop as to that of an uncharged drop. This question has been carefully studied and definitely answered in the affirmative by the following work (cf. §§ 6 and 10).

3. THE SPEEDS v_1 AND v_2.

The accuracy previously attained in the measurement of the times of ascent and descent between fixed cross-hairs was altogether satisfactory, but the method which had to be employed for finding the magnifying power of the optical system, *i. e.*, for finding the actual distance of fall of the drop in centimeters, left something to be desired. This optical system was before a short-focus telescope of such depth of focus that it was quite impossible to obtain an accurate measure of the distance between the cross-hairs by simply bringing a standard scale into sharp focus immediately after focusing upon a drop. Accordingly, as stated in the original article, the standard scale was set up at the exact distance from the telescope of the pin-hole through which the drop entered the field. This distance could be measured with great accuracy but *the procedure assumed that the drop remained exactly at this distance throughout the whole of any observation, sometimes of several hours duration.* But if there were the slightest lack of parallelism between gravity and the lines of the electric field the drop would be obliged to drift slowly, and always in the same direction, away from this position, and a drift of 5 mm. was enough to introduce an error of 1 per cent. Such a drift could in no way be noticed by the observer if it took place in the line of sight; for the speeds of the drops were changing *very slowly* anyway because of evaporation, fall in the potential of the battery, etc., and a change in time due to such a drift would be completely masked by other causes of change. This source of uncertainty was well recognized at the time of the earlier observations and steps were taken at the beginning of the present work to eliminate it. It was in fact responsible for an error of nearly two per cent.

A new optical system was built, consisting of an achromatic objective of 28 mm. aperture and 12.5 cm. focal length and an eyepiece of 12 mm. focal length. The whole system was mounted in a support which could be moved bodily back and forth by means of a horizontal screw of ½ mm. pitch. In an observation the objective was 25 cm. distant from the drop, which was kept continually in sharp focus by advancing or withdrawing the whole telescope system. The depth of focus was so small that a motion of ½ mm. blurred badly the image of the drop. The eyepiece

was provided with a scale having 80 horizontal divisions and the distance between the extreme divisions of this scale (the distance of fall in the following experiments) could be regularly duplicated with an accuracy of at least 1 part in 1,000, by bringing a standard scale (Société Genevoise) into sharp focus. (The optical path when the scale was viewed was made exactly the same as when the drop was viewed.) The distance of fall, then, one of the most uncertain factors of the preceding determination, was now known with at least this degree of precision.

The accuracy of the *time* determinations can be judged from the data in Tables IV.–XIX. On account of the great convenience of a direct-reading instrument these time measurements were all made, not with a chronograph, as heretofore, but with a Hipp chronoscope which read to 0.002 second. This instrument was calibrated by comparison with the standard Ryerson Laboratory clock under precisely the same conditions as those under which it was used in the observations themselves and found to have an error between 0 and 0.2 per cent. depending upon the time interval measured. For the sake of enabling others to check all the computations herein contained if desired, as well as for the sake of showing what sort of consistency was attained in the measurement of time intervals there are given in Table II. the calibration readings for the 30 sec. interval and in Table III. the results of similar readings for all the intervals used.

TABLE II.

Chronoscope Readings for 30 Sec. Interval.	
29.962	29.990
29.988	29.958
29.986	29.920
29.930	29.972
29.964	29.976
30.002	30.006
29.940	29.979
29.998	30.018
29.930	29.926
29.967	29.972
Corr'n = +.1 per cent.	

TABLE III.

Clock Interval, Sec.	Chronoscope Interval.	Corr'n Applied, Per Cent.
6	6.0146	−0.26
10	10.0018	0.00
16	16.0080	0.00
20	19.9835	+0.07
30	29.9695	+0.10
40	39.9436	+0.14
60	59.9072	+0.16
114	113.795	+0.20
120	119.782	+0.20

The change in the per cent. correction with the time interval employed is due to the difference in the reaction times of the magnet and spring contact at make (beginning) and at break (end). All errors of this sort are obviously completely eliminated by making the calibration observations under precisely the same conditions as the observations on the drop. In Tables IV. to XIX. the recorded times are the uncorrected chronograph

readings. The corrections are obtained by interpolation in the last column of Table III.

Under the head of possible uncertainties in the velocity determinations are to be mentioned also the effects of a distortion of the drop by the electric field. Such a distortion would increase the surface of the drop, and hence the speed imparted to it per dyne of *electric* force would not be the same as the speed imparted per dyne of gravitational force when the field was off and the drop had the spherical form. The following observations were made in such a way as to bring to light such an effect if it were of sufficient magnitude to exert any influence whatever upon the accuracy of the determination of e by this method (cf. §§ 6 and 10).

Similarly objection has been made to the oil-drop method on the ground that, on account of internal convection, fluid drops would not move through air with the same speed as solid drops of like diameter and mass. Such objection is theoretically unjustifiable in the case of oil drops of the sizes here considered.[1] Nevertheless the experimental demonstration of its invalidity is perhaps worth while and is therefore furnished below.

4. THE RADIUS "a."

The radius of the drop enters only into the correction term (see equation 4) and so long as this is small need not be determined with a high degree of precision. It is most easily obtained by the following procedure which differs slightly from that originally employed (l. c., p. 379).

It will be seen that the equation (l. c., p. 353)

$$\frac{v_1}{v_2} = \frac{mg}{Fe - mg} \tag{6}$$

contains no assumption whatever save that a given body moves through a given medium with a speed which is proportional to the force acting upon it. Substitution in this equation of $m = \frac{4}{3}\pi a^3(\sigma - \rho)$ and the solution of the resulting equation for a gives

$$a = \sqrt[3]{\frac{3Fe}{4\pi g(\sigma - \rho)} \frac{v_1}{(v_1 + v_2)}}. \tag{7}$$

The substitution in this equation of an approximately correct value of e yields a with an error but one third as great as that contained in the assumed value of e. The radius of the drop can then be determined from (7) with a very high degree of precision as e becomes more and more accurately known. In the following work the value of e substituted in (7) to obtain a was 4.78×10^{-10} but the final value of e obtained would

[1] Hadamard, Compt. Rendus, 1911.

not have been appreciably different if the value substituted in (7) to obtain a had been 5 per cent. or 6 per cent. in error. The determination of a therefore introduces no perceptible error into the evaluation of e.

5. THE CORRECTION-TERM CONSTANT A.

This constant was before graphically determined (l. c., p. 379) by plotting the values of $e_1^{\frac{1}{2}}$ as ordinates and those of l/a as abscissæ and observing that if we let $x = l/a$, $y = e_1^{\frac{1}{2}}$ and $y_0 = e^{\frac{1}{2}}$ equation (3) may be written in the form

$$y_0(1 + Ax) = y \tag{8}$$

or

$$A = \frac{\frac{dy}{dx}}{y_0} = \frac{\text{slope}}{y\text{ intercept}}. \tag{9}$$

Now even if the slope were correctly determined by the former observations all of the above-mentioned sources of error would enter into the value of the intercept and hence would modify the value of A.

As a matter of fact however the accuracy with which the slope itself was determined could be much improved, for with the preceding arrangement it was necessary to make all the observations at atmospheric pressure and the only way of varying l/a was by varying a, *i. e.*, by using drops of different radii. But when a was very small the drops moved exceedingly slowly under gravity and the minutest of residual convection currents produced relatively large errors in the observed speeds, *i. e.*, in e_1. If for example the time of fall over a distance of 2 mm. is 20 minutes it obviously requires an extraordinary degree of stagnancy to prevent a drift in that time of say .2 mm. due to convection. But this would introduce an error of 10 per cent. into e_1. Furthermore with these slow drops Brownian movements introduce errors which can only be eliminated by taking a very large number of readings[1] and this is not in general feasible with such drops. It is quite impossible then by working at a single pressure to obtain from the graph mentioned above a line long enough (l. c., p. 379) to make the determination of its slope a matter of great precision. Accordingly in the new observations the variation of l/a was effected chiefly through the variation of l, *i. e.*, of the pressure p, rather than of a. This made possible not only the accurate evaluation of e, but also the solution of the interesting question as to the law of fall of a given drop through air at reduced pressures.

[1] Fletcher, PHYS. REV., 33, p. 92, 1911.

6. METHOD OF TESTING THE ASSUMPTIONS INVOLVED IN THE OIL-DROP METHOD.

In order to make clear the method of treatment of the following observations a brief consideration of the assumptions underlying the oil-drop method must here be made. These assumptions may be stated thus:

1. The drag which the medium exerts upon a given drop is unaffected by its charge.

2. Under the conditions of observation the oil drops move through the medium essentially as would solid spheres. This assumption may be split into two parts and stated thus: Neither (*2a*) distortions due to the electric field nor (*2b*) internal convection within the drop modify appreciably the law of motion of an oil drop.[1]

3. The density of oil droplets is independent of their radius down to $a = .00005$ cm.

Of these assumptions (*2a*) is the one which needs the most careful experimental test.[2] It will be seen that it is contained in the fundamental equation of the method (see (7)) which may be written in the form

$$e_n = \frac{mg}{Fv_1}(v_1 + v_2). \tag{10}$$

Or still more conveniently in the form

$$e_n = \frac{mgt_g}{F}\left(\frac{1}{t_g} + \frac{1}{t_F}\right), \tag{11}$$

in which t_g and t_F are the respective time intervals required by the drop to fall under gravity and to rise under the field F the distance between the cross-hairs.

In order to see how the assumption under consideration can be tested let us write the corresponding equation after the same drop has caught n' additional units, namely,

$$e_{n+n'} = \frac{mgt_g}{F}\left(\frac{1}{t_g} + \frac{1}{t_{F'}}\right). \tag{12}$$

The subtraction of (11) from (12) gives

$$e_{n'} = \frac{mgt_g}{F}\left(\frac{1}{t_{F'}} - \frac{1}{t_F}\right). \tag{13}$$

[1] M. Brillouin has in addition suggested (see p. 149, La Théorie du Rayonnement et les Quanta) that the drops may be distorted by the molecular bombardment, but Einstein's reply (l. c., p. 150) to this suggestion is altogether unanswerable, and, in addition, such a distortion, if it existed, would make the value of e given by the oil-drop method *too small* instead of too large.

[2] Professor Lunn has however subjected it to a theoretical study and has in this way demonstrated its validity (PHYS. REV., XXXV., p. 227, 1912).

Now equations (11) and (12) show, since mgt_g/F remains constant, that as the drop changes charge the successive values of its charge are proportional to the successive values assumed by the quantity $(1/t_g + 1/t_F)$ and the elementary charge itself is obviously this same constant factor mgt_g/F multiplied by *the greatest common divisor* of all these successive values. It is to be observed too that since $1/t_g$ is in these experiments generally large compared to $1/t_F$ the value of this greatest common divisor, which will be denoted by $(1/t_g + 1/t_F)_0$, is determined primarily by the time of fall *under gravity*, and is but little affected by the time in the field. On the other hand equation (13) shows that the greatest common divisor of the various values of $(1/t_F' - 1/t_F)$, which will be designated by $(1/t_F' - 1/t_F)_0$, when multiplied by the same constant factor mgt_g/F, is also the elementary electrical charge. In other words $(1/t_g + 1/t_F)_0$ and $(1/t_F' - 1/t_F)_0$ are one and the same quantity, but while the first represents essentially a speed measurement when the field is off, the second represents a speed measurement in a powerful electric field. If then the assumption under consideration is correct we have two independent ways of obtaining the quantity which when multiplied by the constant factor mgt_g/F is the elementary electrical charge, but if on the other hand the distortion of the drop by the field modifies the law of motion of the oil drop through the medium then $(1/t_g + 1/t_F)_0$ and $(1/t_F' - 1/t_F)_0$ will not be the same. Now *a very careful experimental study of the relations of* $(1/t_g + 1/t_F)_0$ and $(1/t_F' - 1/t_F)_0$ *shows so perfect agreement that no effect of distortion in changing measurably the value of e can be admitted.*[1] (See Tables IV. to XIX.)

Turning next to assumption (1), this can be tested in three ways, all of which have been tried with negative results. First a drop containing from one up to six or seven elementary charges can be completely discharged and its time of fall under gravity when uncharged compared with its time when charged. Second, the multiple relationships shown in the successive charges carried by a given drop may be very carefully examined. They cannot hold exactly if when the drop is heavily charged it suffers a larger drag from the medium than when it is lightly charged. Third, when drops having widely different charges and different masses are

[1] It may be pointed out in passing that the above discussion brings to light a method of obtaining e which is independent of a viscosity measurement; for $(1/t_F' - 1/t_F)_0$ can be obtained for a body which is heavy enough to be weighed upon a micro-balance. Such a body would fall so rapidly that $1/t_g$ could not be measured, but it could be computed from the measurement of $1/t_F'$ and $1/t_F$ and the equation $(1/t_g + 1/t_F')_0 = (1/t_F' - 1/t_F)_0$. Either (12) or (13) could then be solved for e after m had been determined by direct weighing. A consideration of the sources of error in this method shows however that it cannot be made as accurate as the present method which involves the coefficient of viscosity of air.

brought to the same value of l/a by varying the pressure, the value of e_1 (which is proportional to $(v_1 + v_2)_0$), should come out smaller for the heavily than for the lightly charged drops. The following observations show that this is not the case.

The last criterion is also a test for (2*b*) for if internal convection modifies the speed of fall of a drop as Perrin wishes to assume that it may,[1] it must play a smaller and smaller rôle as the drop diminishes in size, hence varying l/a by diminishing a cannot be equivalent to varying l/a by increasing l. In other words the value of e_1 obtained from work on a large drop at a low pressure should be different from that obtained from work on a small drop at so high a pressure that l/a has the same value as for the large drop.

Finally if the density of a small drop is greater than that of a large one (see assumption 3) then, for a given value of l/a, the small drop will show a larger value of e_1 than the large one inasmuch as the computation of e_1 is based on a constant value of σ. *The fact, then, that for a given value of l/a the value of e_1 actually comes out independent of the radius or charge of the drops shows conclusively either that no one of these possible sources of error exists, or else that they neutralize one another so that for the purposes of this experiment they do not exist.* That they do not exist at all is shown by the independent theoretical and experimental tests mentioned above. This removes I think every criticism which has been suggested of the oil-drop method of determining e and N.

7. Summary of Improvements in Method.

In order to obtain the consistency shown in the following observations it was found necessary to take much more elaborate precautions to suppress convection currents in the air of the observing chamber than had at first been thought needful.

To recapitulate, then, the improvements which have been introduced into the oil-drop method, consist in (1) a redetermination of η; (2) an improved optical system; (3) an arrangement for observing speeds at all pressures; (4) the more perfect elimination of convection; (5) the experimental proof of the correctness of all the assumptions underlying the method, viz., (*a*) that a charge does not alter the drag of the medium on the charged body; (*b*) that the oil drops act essentially like solid spheres; (*c*) that the density of the oil drops is the same as the density of the oil in bulk.

[1] La Théorie du Rayonnement et les Quanta, p. 239—Rapports et Discussions de la Réunion tenue à Bruxelles, Novembre, 1911. Edited by Langevin and de Broglie. Gauthier-Villars.

8. THE EXPERIMENTAL ARRANGEMENTS.

The experimental arrangements are shown in Fig. 1. The brass vessel D was built for work at all pressures up to 15 atmospheres but since the present observations have to do only with pressures from 76 cm. down these were measured with a very carefully made mercury manometer m which at atmospheric pressure gave precisely the same reading as a

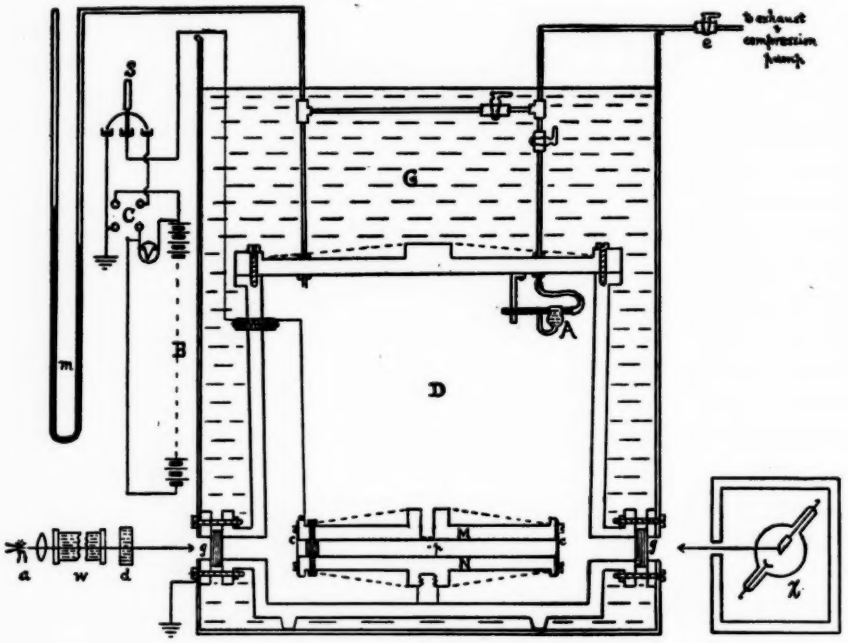


Fig. 1.

standard barometer. Complete stagnancy of the air between the condenser plates M and N was attained first by absorbing all of the heat rays from the arc A by means of a water cell w, 80 cm. long, and a cupric chloride cell[1] d, and second by immersing the whole vessel D in a constant temperature bath G of gas-engine oil (40 liters) which permitted, in general, fluctuations of not more than .02° C. during an observation. This constant temperature bath was found essential if such consistency of measurement as is shown below was to be obtained. A long search for causes of slight irregularity revealed nothing so important as this and after the bath was installed all of the irregularities vanished. The atomizer A was blown by means of a puff of carefully dried and dust-free air introduced through the cock e. The air about the drop p was ionized

[1] See Coblentz, Bulletin of the Bureau of Standards, Washington, D. C., Vol. 7, p. 660, 1911.

when desired by means of Röntgen rays from X which readily passed through the glass window g. To the three windows g (two only are shown) in the brass vessel D correspond, of course, three windows in the ebonite strip c which encircles the condenser plates M and N. Through the third of these windows, set at an angle of about 18° from the line Xpa and in the same horizontal plane, the oil drop is observed.

9. The Observations.

The record of a typical set of readings on a given drop is shown in Table IV. The first column, headed t_g, gives the successive readings on the time of descent under gravity. The fourth column, headed t_{F_a} gives the successive times of ascent under the influence of the field F as measured on the Hipp chronoscope. These two columns contain all the data which is used in the computations. But in order to have a test of the stagnancy of the air a number of readings were also made with a stop-watch on the times of ascent through the first half and through the whole distance of ascent. These readings are found in the second and third columns, the times for the first half under the head $\frac{1}{2}t_{F_a}$, the times for the whole distance under the head t_{F_a}. It will be seen from these readings that there is no indication whatever of convection, since the readings for the one half distance have uniformly one half of the value of the readings for the whole distance, within the limits of error of a stop-watch measurement. This sort of a test was made on the majority of the drops, but since no further use is made of these stop-watch readings they will not be given in succeeding tables.

The fifth column, headed $1/t_F$, contains the reciprocals of the values in the fourth column after the correction found from Tables II. and III. has been applied. The sixth column contains the successive differences in the values of $1/t_F$ resulting from the capture of ions. The seventh column, headed n', contains the number of elementary units caught at each change, a number determined simply by observing by what number the quantity just before it in column 6 must be divided to obtain the constancy shown in the eighth column, which contains the successive determinations of $(1/t_F' - 1/t_F)_0$ (see § 6). Similarly the ninth column, headed n, gives the total number of units of charge on the drop, a number determined precisely as in the case of the numbers in the seventh column by observing by what numbers the successive values of $(1/t_g + 1/t_F)$ must be divided to obtain the constancy shown in the tenth column, which contains the successive values of $(1/t_g + 1/t_F)_0$. Since n' is always a small number and in some of the changes almost always has the value 1 or 2 its determination for any change is obviously never a matter of the slightest

uncertainty. On the other hand, n is often a large number, but with the aid of the known values of n' it can always be found with absolute certainty so long as it does not exceed say 100 or 150. It will be seen from the means at the bottom of the eighth and the tenth columns that in the case of this drop the two ways discussed in § 6 of obtaining the number which when multiplied by mgt_g/F is the elementary electrical charge yield absolutely identical results.

TABLE IV.

Drop No. 6.

t_g Sec.	$\frac{1}{2}t_{F_0}$ Sec.	t_{F_0} Sec.	t_{F_c} Sec.	$\frac{1}{t_F}$	$\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n'	$\frac{1}{n'}\left(\frac{1}{t'_F}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$
11.848	39.9	80.2	80.708	.01236				18	.005366
11.890	11.2	22.4	22.366		.03234	6	.005390		
11.908			22.390	.04470				24	.005371
11.904	11.2	22.4	22.368		.03751	7	.005358		
11.882	70.6	140.4	140.565	.007192	.005348	1	.005348	17	.005375
11.906	39.9	79.6	79.600	.01254				18	.005374
11.838			34.748		.01616	3	.005387		
11.816			34.762	.02870				21	.005376
11.776			34.846						
11.840			29.286	.03414				22	.005379
11.904	14.6	29.3	29.236		.026872	5	.005375		
11.870	69.3	137.4	137.308	.007268	.021572	4	.005393	17	.005380
11.952	17.6	34.9	34.638	.02884				21	.005382
11.860					.01623	3	.005410		
11.846			22.104	.04507				24	.005386
11.912			22.268		.04307	8	.005384		
11.910			500.1	.002000				16	.005387
11.918			19.704	.05079	.04879	9	.005421	25	.005399
11.870			19.668		.03874	7	.005401		
11.888			77.630	.01285				18	.005390
11.894	38.9	77.6	77.806		.01079	2	.005395		
11.878	21.0	42.6	42.302	.02364				20	.005392
11.880					Means		**.005386**		**.005384**

Duration of exp. = 45 min.,
Plate distance = 16 mm.,
Fall distance = 10.21 mm.,
Initial volts = 5,088.8.
Final volts = 5,081.2.
Temperature = 22.82° C.,
Pressure = 75.62 cm.,
Oil density = .9199,
Air viscosity[1] = $1,824 \times 10^{-7}$,
Radius (a) = .000276 cm.,
l/a = .034,
Speed of fall = .08584 cm./sec.,

$e_1 = 4.991 \times 10^{-10}$.

[1] In the above and in all the following tables the computations were made on the basis of the assumption $\eta_{23} = 1,825 \times 10^{-7}$ instead of $\eta_{23} = 1,824 \times 10^{-7}$ (see § 2). The reduction to the latter value has been made only in the final value of e (see § 10).

Table V.

Drop No. 16.

t_g	t_F	$\frac{1}{t_F}$	n'	$\frac{1}{n'}\left(\frac{1}{t'_F}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.638							
18.686							
18.689	17.756	.05628			16	.006853	
18.730	17.778		5	.006908			$V_i=5106$
18.686	45.978	.02174			11	.006832	$V_f=5100$
18.726	45.870						$t=23.7°$ C.
18.772	45.716	.021826			8	.006851	$p=74.68$
18.740	45.758		3	.006795			$v_1=.05449$
18.724	694.0	.001441	5	.006860			$a=.0002188$
18.720	27.95	.03574	4	.006825	13	.006855	$l/a=.04390$
18.816	118.388	.008439	2	.006866	9	.006868	$e_1=5.065$
18.816	45.030	.02217			11	.006867	
18.716	34.564	.02890			12	.006856	
18.804	44.826	.02227			11	.006876	
18.746	117.198	.008518	2	.006876	9	.006876	
18.746	44.784	.022295	2	.006889	11	.006879	
18.790							
18.738				**.006860**		**.006861**	

Table VI.

Drop No. 14.

t_g	t_F	$\frac{1}{t_F}$	n'	$\frac{1}{n'}\left(\frac{1}{t'_F}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.606							
18.732							
18.784							
18.700	46.172	.02163			11	.006820	
18.730	17.896	.05600	5	.006874			$V_i=5077$
18.652	17.818				16	.006833	$V_f=5073$
18.656	46.328		5	.006886			$t=23.09°$ C.
18.730	46.258	.02157			11	.006815	$p=75.28$
18.760	46.266		1	.006803			$v_1=.05451$
18.708	67.473						$a=.0002185$
18.658	67.148	.01484			10	.006823	$l/a=.04348$
18.668	67.148		6	.006840			$e_1=5.064$
18.826	17.896	.05588			16	.006831	
18.710	15.868	.06305			17	.006850	
18.802	15.854		9	.006853			
18.778	730.0	.001370	6	.006882	8	.006845	
18.790	23.376	.04266			14	.006861	
18.846	23.504		4	.006850			
18.804	65.416	.01526	1	.006871	10	.006865	
18.662	118.970	.008389	1	.006784	9	.006864	
18.704	622.8	.001605			8	.006874	
18.730				**.006850**		**.006844**	

In order to show the sort of consistency attained in this work the complete records are given in Tables V., VI., VII., VIII. and IX. of five drops of practically the same size, taken at very nearly the same pressures. These are the only drops of this size which were observed with the present arrangement so that they represent the regular run of observations rather than a selected group. The symbols in the last column V_i, V_f, t, p, v_1, and a stand for initial volts, final volts, temperature, pressure, velocity under gravity, and radius, respectively. It will be seen from the second columns (see Table V.) that in general in spite of the precautions taken against evaporation (l. c., p. 388) the drops do evaporate very slowly, since with a given charge the speed in the field very slowly increases. It is for this reason that the numbers in the next to the last column tend to increase very slightly. This slow change introduces no error into e_1, provided corresponding values of t_g, t_F and V (volts) are combined to obtain e_1. The mean values taken throughout the same time-interval

TABLE VII.

Drop No. 18.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.626						
18.716						
18.602	21.206			15	.006716	
18.634	21.110	5	.006696			
18.694	72.590	2	.006820	10	.006726	$V_i = 5030$
18.678	36.454			12	.006742	$V_f = 5018$
18.598	48.870	2	.006735	11	.006725	$t = 23.0°$ C.
18.612	142.838	1	.006792	9	.006722	$p = 76.06$
18.622	72.428	2	.006732	10	.006729	$v_1 = .05463$
18.795	36.722					$a = .0002191$
18.732	36.652			12	.006729	$l/a = .04290$
18.780	36.602	3	.006719			$e_1 = 5.043$
18.736	140.891	2	.006799	9	.006732	
18.754	48.302					
18.712	48.266	4	.006756	11	.006745	
18.760	20.942			15	.006747	
18.716						
18.740						
18.695			**.006753**		**.006731**	

constitute such corresponding values. On account of this slow change, however, the readings from which the differences $(1/t_F' - 1/t_F)$ are taken should be separated by as small a time interval as possible. It is for this reason that in Table V., for example, to obtain the difference $(1/t_F' - 1/t_F)$ corresponding to the change from $t_F = 45$ sec. to $t_F = 694$ sec.

TABLE VIII.

Drop No. 15.

t_g	t_F	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.908				
18.948	14.348		.006801	
18.958	14.352	.006790		
18.950	45.070		.006813	
18.904	34.338			$V_i=5085$
18.988	34.432		.006816	$V_f=5071$
18.896	34.334			$t=23.83°$ C.
19.094	44.864			$p=75.24$
18.936	34.430	.006807		$v_1=.05274$
18.980	548.0	.006858	.00620	$a=.0002182$
19.030	34.14			$l/a=.04368$
18.872	44.654			$e_1=5.040$
18.808	44.520		.006831	
18.910	44.526			
18.946	64.28	.006766		
18.936	114.404		.006834	
18.950	113.452	.006751		
19.030	63.934	.006728	.006835	
19.116	23.260		.006832	
19.018	23.350			
18.959		**.006817**	**.006823**	

TABLE IX.

Drop No. 17.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.402						
18.556						$V_i=5065$
18.350	14.966			18	.006752	$V_f=5055$
18.470	14.870	6	.006727			$t=23.06°$ C.
18.412	37.376					$p=73.47$
18.318	37.594			12	.006748	$v_1=.05545$
18.388	37.368					$a=.0002209$
18.376	50.228	1	.006780	11	.006749	$e/a=.04411$
18.406	76.154	1	.006780	10	.006742	$e_1=5.054\times10^{-10}$
18.392	155.6	1	.006682	9	.006749	
18.492						
18.415			.006742		.006748	

the last two of the 45 sec. readings are averaged instead of the whole four. It is worthy of note, too, in this connection that if a change in the time in the field takes place first from 45 sec. to 694 sec. and then im-

TABLE X.

Drop No. 42.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.360						
18.362						
18.328	45.378			11	.006960	
18.444	45.208	6	.007027			
18.442	15.574			17	.006983	
18.330	17.468	6	.007011	16	.006983	$V_i=4240$
18.330	66.000					$V_f=4236$
18.428	66.020			10	.006965	$t=22.94°$ C
18.174	122.600	1	.006993			$p=15.72$ cm.
18.388	45.414	2	.006951	9	.006962	$v_1=.05564\ \frac{\text{cm.}}{\text{sec.}}$
18.392	45.282					
18.240	45.110			11	.006960	$a=.0002060$ cm.
18.314	45.282					$l/a=.2210$
18.324	121.600	2	.006911			
18.312	121.200			9	.006971	$e_1=\mathbf{6.244\times10^{-10}}$
18.390						
18.347			**.006978**		**.006969**	

TABLE XI.

Drop No. 46.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
25.856	10.334			19	.007121	
25.946	10.342	10	.007086			
25.890	38.604	1	.007195	9	.007159	
25.876	53.450	3	.007152	8	.007154	
25.818	24.906			11	.007152	
25.934	30.248					$V_i=3406$
25.956	30.016	3	.007183	10	.007172	$V_f=3396$
25.876	18.282			13	.007174	$t=22.81°$ C.
26.064	16.216			14	.007159	$p=14.68$ cm.
26.018	24.860			11	.007161	$v_1=.03937$ cm.
25.902	21.062	2	.007155	12	.007168	$a=.0001690\ \frac{\text{cm.}}{\text{sec.}}$
25.860	30.126	2	.007155	10	.007171	
25.930	20.884					$l/a=.2886$
25.994	21.130					$e_1=\mathbf{6.719\times10^{-10}}$
25.814	21.174	5	.007170			
26.012	85.922	1	.007198	7	.007167	
25.904	226.600	1	.007148	6	.007159	
25.802	86.368			7	.007174	
25.918	86.406					
25.816						
25.909			**.007160**		**.007161**	

mediately back again to the 45 second value the mean of the two values of $(1/t_F' - 1/t_F)$ thus obtained is independent of any error arising from the evaporation of the drop. For this reason the mean value of the quantity $1/n'(1/t_F' - 1/t_F)$ is in general much more trustworthy than might be inferred from the variation in the individual numbers from which this mean is obtained.

TABLE XII.

Drop No. 53.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
33.432	28.494			10	.006491	
33.346	28.624	2	.006501			$V_i = 2463$
33.172	20.806			12	.006493	$V_f = 2440.2$
33.310	20.832	3	.006503			$t = 23.16°$ C.
33.380	35.032	1	.006490	9	.006491	$p = 12.61$
33.306	28.548	4	.006505	10	.006491	$v_1 = .03055$
33.346	111.244	1	.006471	6	.006482	$a = .0001439$
33.328	400.000	1	.006436	5	.006485	$l/a = .3945$
33.684	111.706			6	.006475	$e_1 = 7.450 \times 10^{-10}$
33.484						
33.379			**.006484**		**.006487**	

TABLE XIII.

Drop No. 48.

t_g	t_F	$\frac{1}{t_F}$	n'	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
32.366	20.330	.04919			13	.006157	$V_i = 2561.$
32.398	23.140	.04313			12	.006165	$V_f = 2557.$
32.217	23.230		5	.006164			$t = 22.81°$ C.
32.342	80.786	.01231			7	.006166	$p = 15.35$ cm.
32.358	81.416		7	.006137			$v_1 = .03150$
32.438	18.113	.05517			14	.006144	$a = .0001501$ cm.
32.412	18.144		6	.006142			$l/a = .3104$
32.236	54.490	.01832			8	.006147	$e_1 = 6.866 \times 10^{-10}$
32.424	81.486	.01224	1	.006080	7	.006156	
32.356				**.006131**		**.006156**	

Nevertheless in practically all of the following work in view of the large number of observations in the t_g column, the mean at the bottom of the column $1/n(1/t_g + 1/t_F)$ is considered more trustworthy than the mean at the bottom of the column $1/n'(1/t_F' - 1/t_F)$ and it has been in fact exclusively used in the computation of e_1. Only in the case of 2 or 3 of the fastest drops (Tables XVI. and XVII.) are the uncertainties in

TABLE XIV.

Drop No. 47.

t_g	t_F	$\frac{1}{t_F}$	n'	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
12.836	11.960	.08369			42	.003840	
12.994	11.938						
12.892	10.704		13	.003812			
12.914	29.350						
12.930	29.280	.03411			29	.003851	
12.902	29.108						
12.838	32.866						$V_i = 2555.$
12.808	33.068						$V_f = 2545.$
12.920	32.894	.03034			28	.003854	$t = 22.83°$ C.
12.886	32.892						$p = 9.70$ cm.
12.908	29.204		5	.003858			$v_1 = .07921$ cm./sec.
12.902	32.950						$a = .0002380$ cm.
12.916	90.040	.01108			23	.003855	$l/a = .3097$
12.850	90.152		1	.003860			$e_1 = 6.841 \times 10^{-10}$
12.854	66.762	.01496			24	.003854	
12.912	66.650		2	.003898			
12.908	139.8	.00716			22	.003852	
12.870	139.4		2	.003878			
12.882	66.942	.01492			24	.003855	
12.891				**.003861**		**.003852**	

TABLE XV.

Drop No. 41.

t_g	t_F	$\frac{1}{t_F}$	n'	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
24.016	42.188						
24.142	42.078	.02369			8	.009336	
24.130	42.098		1	.009380			
24.070	69.900	.01431			6	.009328	$V_i = 5065$
24.000	203.200	.004921	1	.009389	5	.009316	$V_f = 5059$
24.030	23.844	.04194	4	.009255	9	.009286	$t = 23.05°$ C.
24.046	30.606				8	.009289	$p = 19.01$ cm.
24.028	42.800						$v_1 = .04253$
23.968	42.944	.02326			7	.009276	$a = .0001816$
24.018	71.400	.01400	1	.009260	6	.009277	$l/a = .1394$
23.770			2	.009295			$e_1 = 6.097 \times 10^{-10}$
23.882	30.652	.03259				.009282	
24.008				**.009314**		**.009301**	

$(1/t_g + 1/t_F)_0$ greater perhaps than those in $(1/t_F' - 1/t_F)_0$ and in these cases the two were so near together that there was no object in using the latter instead of the former. It should be stated that all time intervals

longer than 150 sec. were measured with the stop-watch rather than with the chronoscope and are not subjected to the corrections in Tables II. and III. In general, too, only differences in $t_F' - t_F$ amounting to as much as 20 seconds are used for the determination of $(1/t_F' - 1/t_F)$ since obviously the observational error is large when $t_F' - t_F$ is small.

TABLE XVI.

Drop No. 1.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_F'} - \frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g} + \frac{1}{t_F}\right)$	
	17.514			89	.003235	
	17.500	11	.003244			
	46.724			78	.003233	
	46.494	10	.003216			
4.346	18.722			88	.003233	
4.400	18.616	11	.003256		.003228	
4.310	56.280			77		$V_i = 5174$
4.376	56.276	9	.003217			$V_f = 5162$
4.370	21.362			86	.003227	$t = 23.00°$ C.
4.422	21.476					$p = 75.80$ cm.
4.392						$v_1 = .23565 \frac{\text{cm.}}{\text{sec.}}$
4.290	58.936					
4.392	58.194			77	.003219	$a = .0005856$
4.360	58.456					$l/a = .01615$
4.346	58.904					$e_1 = 4.877 \times 10^{-10}$
4.368	20.412	10	.003199			
4.350	20.404			87	.003216	
4.363	20.322					
corrected to	10.710			101	.003211	
	10.660					
	20.290			87	.003218	
	20.296					
4.328[1]			**.003226**		**.0032245**	

A study of Tables IV. to IX. shows, *first*, a striking agreement between the values of $(1/t_F' - 1/t_F)_0$ and $(1/t_g + 1/t_F)_0$ the largest divergence being found in Table V. where it amounts to 0.3 per cent., and *second*, a satisfactory agreement between the values of e_1 obtained from the different

[1] These corrected times in Tables XVI. and XVII. are obtained by a slight extrapolation upon a calibration curve plotted from Table III. These two drops are the largest used and fall too rapidly for the most accurate work, but were introduced so as to test as thoroughly as possible the assumptions that even the largest of these drops fall like rigid spheres and that heavily charged drops experience no more drag from the medium than do uncharged ones. The drop of Table XVII. is evaporating more rapidly than any other used (see column t_F), probably because of the low pressure (4.46 cm.), hence the fourth column numbers are here obtained only from immediately adjacent observations in the second column. Each of these fourth column numbers shows the influence of the evaporation, but it is interesting to see how it is eliminated from the mean.

drops of approximately the same size, the largest divergence from the mean value being here too 0.3 per cent.

TABLE XVII.

Drop No. 56.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
5.092	19.480					
5.010	19.356			136	.001837	
5.082	19.374					
5.044	19.202					
— —	29.214			127	.001832	
	29.022					
5.044	28.686					$V_i=1701$
5.030	38.688			122	.001839	$V_f=1699$
	38.620	7	.001786			$t=23.21°$ C.
5.066	75.136					$p=4.46$ cm.
5.120	73.752			117	.001811	$v_1=.20256$
5.046	72.758	9	.001837			$a=.0003653$ cm.
5.128	33.034					
				126	.001814	$l/a=.4396$
4.912	32.788					
5.036	39.956			123	.001814	$e_1=7.777\times10^{-10}$
5.080	46.790	5	.001796	121	.001814	
5.122	80.820			116	.001816	
5.058	80.152	3	.001877			
cor'd to	55.206	6	.001823	119	.001810	
	34.398			125	.001818	
5.039[1]			.001824		.001821	

TABLE XVIII.

Drop No. 22.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
40.518	17.760	4	.01012	8	.01012	
40.522	63.100			3	.01015	$V_i=5009$
40.382						$V_f=5001$
40.542						$t=23.22°$ C.
40.650	15.138			9	.01009	$p=76.42$ cm.
40.696	27.716			6	.01011	$v_1=.02515$
40.478	15.060	4	.01011	9		$a=.0001475$
40.458	38.606			5	.01012	$l/a=.06350$
40.494	38.382	2	.01008			$e_1=5.168\times10^{-10}$
40.802	172.626				.01013	
40.542			.01010		.01012	

A few typical records of observations made at different pressures (see "p," last column) and on drops of different sizes (see "a," last column) are presented in Tables X to XIX.

TABLE XIX.

Drop No. 52.

t_0	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_0}+\frac{2}{t_F}\right)$	
50.364						$V_i=3362$
50.442	44.446	1	.010515	4	.010566	$V_f=3340$
50.416	30.254			5	.010556	$t=22.98$
50.770	30.326					$p=16.95$
50.178	22.904			6	.010575	$v_1=.020216$
50.456	30.396	2	.01047	5	.010532	$a=.0001183$
50.460	83.716	1	.010664	3	.010573	$l/a=.3568$
50.118	796.000			2	.010528	$e_1=7.210\times10^{-10}$
50.400			**.01055**		**.010555**	

Table XX. contains a complete summary of the results obtained on all of the 58 different drops upon which complete series of observations like the above were made during a period of 60 consecutive days. It will be seen from this table that these observations represent a 30-fold variation in l/a (from .016, drop No. 1, to .444, drop No. 58), a 17-fold variation in p (from 4.46 cm., drop No. 56, to 76.27 cm., drop No. 10), a 12-fold variation in a (from 4.69×10^{-5} cm., drop No. 28, to 58.56×10^{-5} cm., drop No. 1) and a variation in the number of free electrons carried by the drop from 1 on drop No. 28 to 136 on drop No. 56. The time of fall of drop No. 28 was also tested when it was completely discharged, as have been the times of many other drops which carried most of the time but one electron.

Much larger variations both in a and p, and therefore in l/a, might have been used, and have in fact been used, for finding the law of fall of a drop through rarefied air, but for the end here sought, namely, the most accurate possible determination of e, it was found desirable to keep the t_0 interval for the most part between the limits 10 sec. and 40 sec., in order to avoid chronograph errors on the one hand and Brownian movement irregularities on the other. That neither of these sources of error is appreciable in these observations may be seen from a study of Tables IV.–XIX., which are thoroughly representative of the work on all the drops.

10. RESULTS AND DISCUSSION.

It will be seen at once from equation (4) that the value of e is simply the value of e_1 for which $l/a = 0$, so that if successive values of $e_1^{\frac{1}{3}}$ are plotted as abscissæ and of l/a as ordinates the intercept of the resulting curve on the $e_1^{\frac{1}{3}}$ axis is $e^{\frac{1}{3}}$. Furthermore if A is a constant then the curve in question is a straight line and A is the slope of this line divided by the

TABLE XX.

No.	Tem. °C.	P.D. (Volts).	t_g (Sec.).	V_1 cm./sec.	$(V_1+V_2)_0$	n	$a\times10^5$ cm.	p (cm. Hg).	$1/pa$	l/a	$e_1\times10^{10}$	$e_1^{\frac{3}{2}}\times10^8$	$e^{\frac{3}{2}}\times10^8$	
1	23.00	5,168	4.363	.2357	.003293	77–102	58.56	75.80	22.52	.01615	4.877	61.90	61.14	
2	22.80	5,120	8.492	.1202	.004670	27–36	32.64	75.00	40.85	.02933	4.981	62.82	61.26	
3	23.46	5,100	9.905	.1032	.004996	22–27	30.29	73.71	44.88	.03212	4.971	62.75	61.04	
4	22.85	5,163	10.758	.09489	.005211	18–36	28.94	75.20	45.92	.03288	5.001	63.00	61.24	
5	23.08	5.072	10.663	.09575	.005176	20–30	29.14	73.25	46.85	.03353	4.982	62.82	61.13	
6	22.82	5,085	11.880	.08584	.005497	17–24	27.54	75.62	48.11	.03437	4.991	62.93	61.09	
7	23.79	5,090	11.950	.08368	.005480	19–22	27.57	75.10	48.44	.03466	4.981	62.82	61.07	
8	23.50	5,158	12.540	.08141	.005623	16–19	26.90	75.30	49.52	.03544	5.016	63.12	61.23	
9	22.87	5,139	13.562	.07375	.005962	19–23	25.71	75.00	51.73	.03702	5.016	63.13	61.15	
10	23.25	5,015	15.380	.06641	.006174	13–22	24.31	76.27	54.09	.03871	5.010	63.08	61.02	
11	23.01	5,066	15.193	.06720	.006087	11–14	24.36	73.90	55.52	.03973	5.015	63.12	61.00	
12	23.00	5,080	15.985	.06375	.006416	12–16	23.70	75.14	56.15	.04018	5.028	63.24	61.10	
13	23.00	5,024	15.695	.05463	.006873	9–15	21.91	76.06	59.94	.04290	5.043	63.35	61.06	
14	23.09	5,077	18.730	.05451	.006988	8–16	21.85	75.28	60.78	.04348	5.064	63.53	61.21	
15	23.85	5,078	18.959	.05274	.006966	8–18	21.78	75.24	61.03	.04368	5.040	63.33	61.07	
16	23.70	5,103	18.738	.05449	.007005	9–16	21.87	74.68	61.33	.04390	5.065	63.54	61.21	
17	23.06	5,060	18.415	.05545	.006890	9–18	22.06	73.47	61.69	.04411	5.054	63.43	61.00	
18	22.83	5,093	26.130	.03907	.008339	5–13	18.45	75.54	71.74	.05134	5.098	63.82	61.08	
19	22.95	5,033	28.568	.03570	.008651	5–9	17.63	75.87	74.77	.05350	5.120	64.00	61.12	
20	23.00	5,094	9.480	.10772	.005058	23–32	30.54	41.77	78.40	.05612	5.145	64.22	61.23	
21	23.08	5,018	35.253	.02893	.009660	4–11	15.80	74.32	85.08	.06089	5.166	64.36	61.11	
22	23.22	5,005	40.542	.02515	.010332	3–9	14.75	76.42	88.70	.06350	5.168	64.40	61.01	
23	22.76	5,098	39.900	.02554	.010510	3–6	14.85	75.40	89.35	.06395	5.190	64.59	61.18	
24	23.16	5,050	12.466	.08189	.005896	15–28	26.44	37.19	101.8	.07283	5.269	65.24	61.35	
25	22.98	5,066	15.157	.06737	.006399	12–17	24.01	38.95	107.2	.07660	5.278	65.28	61.20	
26	23.20	4,572	7.875	.12980	.004324	33–40	33.07	24.33	124.4	.08892	5.379	66.06	61.31	
27	23.18	4,570	9.408	.1085	.004730	23–29	30.23	25.37	130.4	.09330	5.381	66.16	61.18	
28	23.00	5,145	84.270	.1211	.01595	1–4	4.69	75.83	130.3	.09322	5.379	66.14	61.16	
29	22.99	5,073	23.223	.04393	.008488	6–12	19.06	33.47	156.8	.1117	5.529	67.36	61.37	

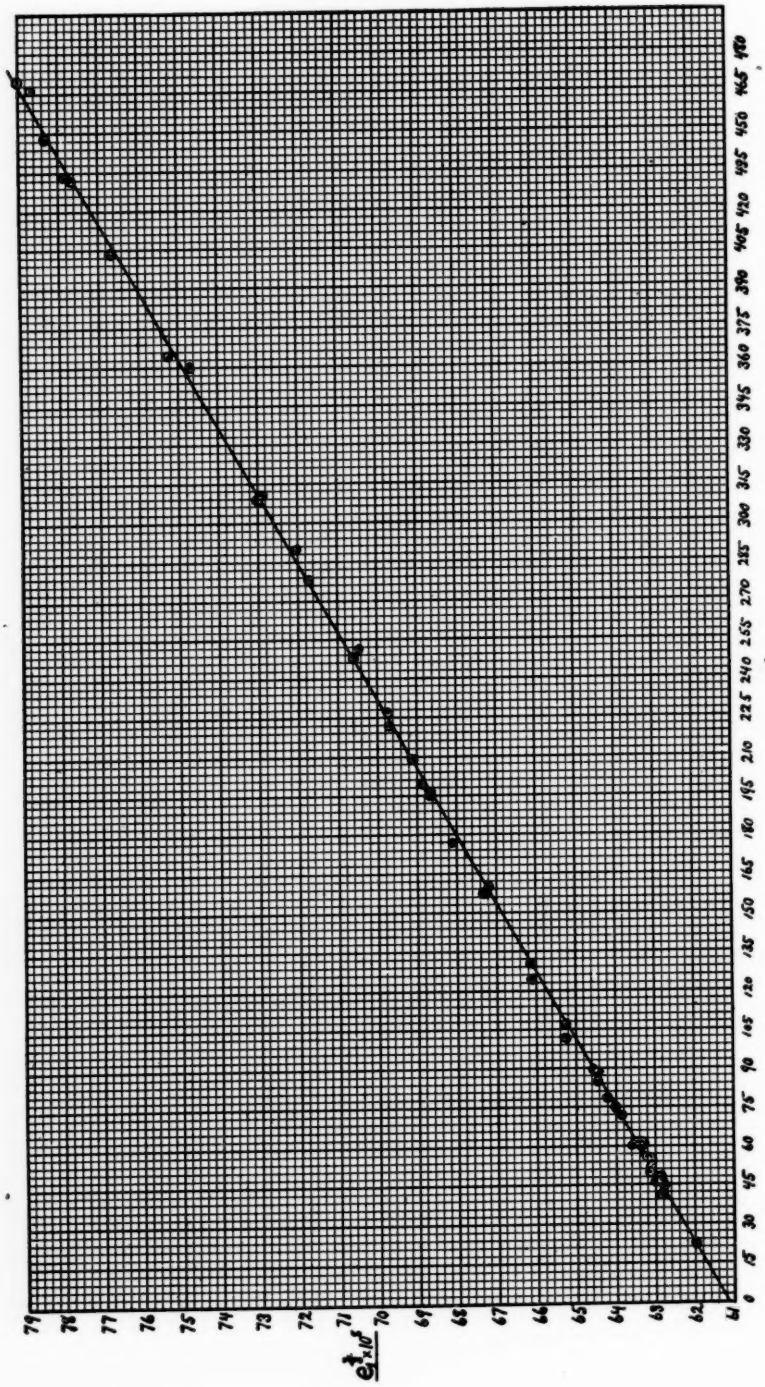
Mean = 61.120

Mean = 61.138

No.	Tem. ° C.	P.D. (Volts).	t_g (Sec.).	V_1 cm./sec.	$(V_1+V_2)_0$	n	$a\times10^5$ cm.	p (cm. Hg).	$1/pa$	l/a	$e_1\times10^{10}$	$e_1^{\frac{2}{3}}\times10^8$	$e^{\frac{2}{3}}\times10^8$	
30	23.19	5,090	26.830	.03801	.009111	5–10	17.77	35.18	160.2	.1147	5.507	67.18	61.06	
31	22.89	5,098	38.479	.02649	.011180	3–5	14.71	36.51	176.5	.1263	5.621	68.12	61.38	
32	23.06	5,070	14.060	.07246	.006762	12–17	24.29	21.12	195.0	.1394	5.692	68.67	61.22	
33	23.07	4,582	18.229	.05601	.006981	10–13	21.33	23.86	196.6	.1405	5.687	68.64	61.13	
34	23.06	5,061	38.010	.02682	.011205	3–8	14.72	34.01	199.8	.1429	5.714	68.84	61.20	
35	23.00	4,246	9.265	.11032	.004653	27–34	29.84	16.00	209.5	.1499	5.739	69.07	61.07	
36	22.91	4,236	9.879	.10340	.004863	24–28	28.74	15.67	222.0	.1589	5.820	69.71	61.23	
37	23.06	4,236	12.040	.08496	.005362	18–24	26.27	16.75	227.5	.1625	5.821	69.72	61.03	
38	22.94	2,556	10.657	.09581	.003109	32–43	27.49	14.70	247.5	.1771	5.935	70.61	61.16	
39	23.00	5,054	19.950	.05115	.008370	8–15	20.12	19.73	251.8	.1802	5.910	70.41	60.79	
40	23.09	5,058	21.130	.04830	.008865	7–9	18.38	18.54	278.3	.1993	6.076	71.72	61.09	
41	23.05	5,062	24.008	.04254	.009496	6–8	18.16	19.01	289.6	.2073	6.110	72.03	60.97	
42	22.94	4,238	18.347	.05564	.007110	9–17	20.60	15.72	308.8	.2210	6.224	73.04	61.24	
43	23.18	3,254	13.909	.07340	.004729	16–28	23.70	13.55	311.0	.2227	6.214	72.83	60.95	
44	23.04	4,231	29.114	.03503	.009273	5–9	16.16	17.17	360.6	.2579	6.466	74.77	61.00	
45	22.97	3,317	29.776	.03425	.007430	5–12	15.90	17.27	364.2	.2606	6.537	75.30	61.39	
46	22.81	3,401	25.909	.03937	.007311	6–19	16.90	14.68	403.3	.2886	6.719	76.71	61.30	
47	22.83	2,550	12.891	.07921	.003935	18–42	23.80	9.70	432.8	.3097	6.841	77.66	61.13	
48	22.80	2,559	32.326	.03150	.006286	7–14	15.01	15.35	433.8	.3104	6.866	77.85	61.28	
49	23.02	3,370	14.983	.06815	.011353	8–9	22.00	10.10	448.8	.3221	6.936	78.36	61.22	
50	23.45	2,535	11.659	.08757	.003783	25–30	24.88	8.60	466.7	.3340	6.978	78.67	60.85	
51	23.48	2,539	10.924	.09346	.003615	27–34	25.69	8.26	470.7	.3368	7.024	79.02	61.04	
52	22.98	3,351	50.400	.02021	.010775	2–6	11.83	16.95	498.5	.3568	7.210	80.40	61.36	
53	23.16	2,451	33.379	.03055	.006623	5–10	14.39	12.61	551.3	.3945	7.470	82.19	61.13	
54	23.46	2,533	19.227	.05347	.005314	11–17	18.87	9.03	587.8	.4112	7.661	83.73	61.18	
55	22.90	2,546	24.254	.04206	.006041	9–18	16.72	10.11	591.5	.4233	7.672	83.82	61.22	
56	23.21	1,700	5.058	.20256	.001861	117–136	36.53	4.46	614.2	.4396	7.777	84.57	61.11	
57	23.12	2,321	15.473	.06599	.004360	18–24	20.85	7.74	619.7	.4435	7.774	84.54	60.87	
58	23.03	3,388.5	24.33	.04196	.008183	6–10	16.62	9.070	620.2	.4439	7.810	84.83	61.14	

Mean = 61.138

Mean of all numbers in last column = 61.138
Mean of first 23 numbers = 61.120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$\frac{1}{Pa}$

Fig. 2.

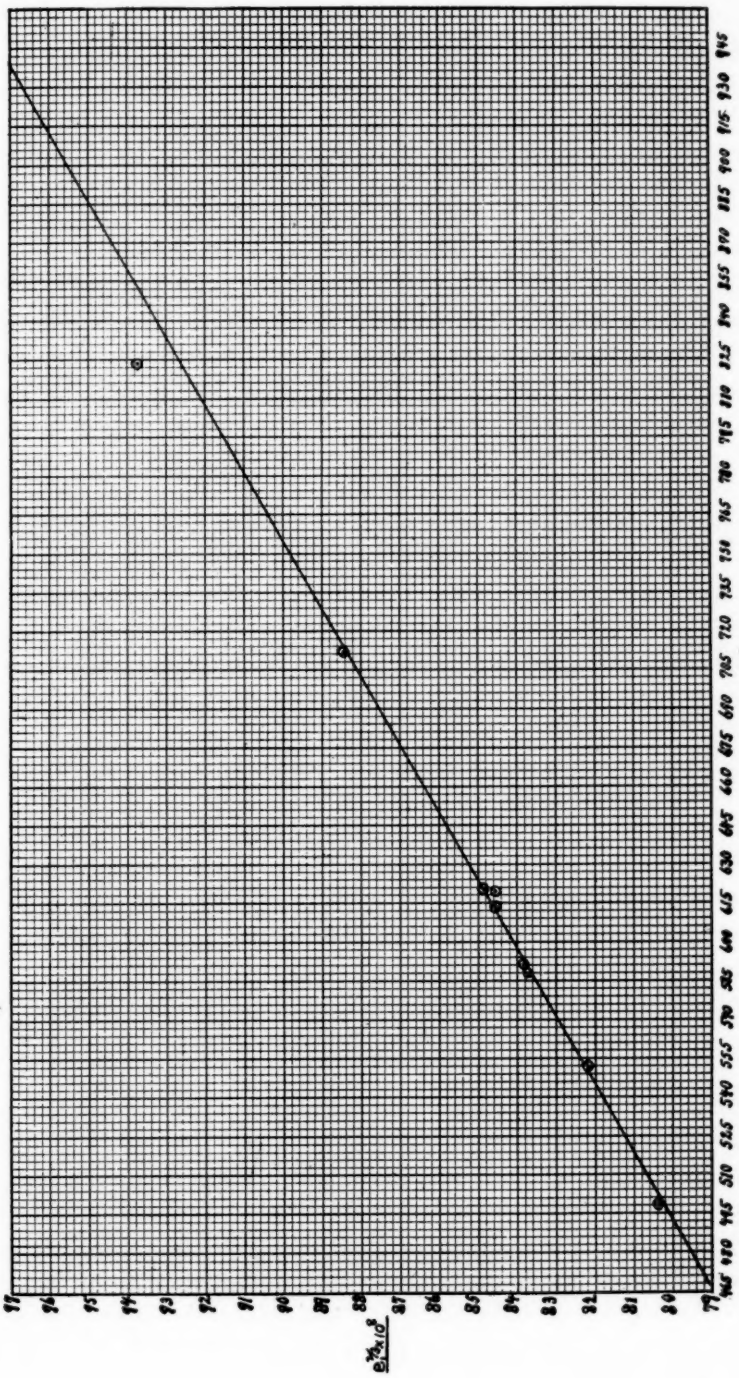

Fig. 3.

y intercept (see equation 9). In view of the uncertainty in l due to the fact that k in the equation $\eta = knm\bar{v}l$ has never been exactly evaluated, it was thought preferable to write the correction term to Stokes's law (see (2 and 3) in the form $(1 + b/pa)^{-1}$ instead of in the form $(1 + Al/a)^{-1}$ and then to plot $e_1^{\frac{3}{2}}$ against $1/pa$. Nevertheless in view of the greater ease of visualization of l/a all the values of this quantity corresponding to successive values of $1/pa$ are given in Table XX., k being taken, merely for the purposes of this computation, as .3502 (Boltzmann). Fig. 2 shows the graph obtained by plotting the values of $e_1^{\frac{3}{2}}$ against $1/pa$ for the first 51 drops of Table XX., and Fig. 3 shows the extension of this graph to twice as large values of $1/pa$ and $e_1^{\frac{3}{2}}$. It will be seen that there is not the slightest indication of a departure from a linear relation between $e_1^{\frac{3}{2}}$ and $1/pa$ up to the value $1/pa = 620.2$ which corresponds to a value of l/a of .4439 (see drop No. 58, Table XX.). Furthermore the scale used in the plotting is such that a point which is one division above or below the line in Fig. 2 represents in the mean an error of 2 in 700. *It will be seen from Figs. 2 and 3 that there is but one drop in the 58 whose departure from the line amounts to as much as 0.5 per cent. It is to be remarked, too, that this is not a selected group of drops but represents all of the drops experimented upon during 60 consecutive days*, during which time the apparatus was taken down several times and set up anew. It is certain then that an equation of the form (2) holds very accurately up to $l/a = .4$. The last drop in Fig. 3 seems to indicate the beginning of a departure from this linear relationship. Since such departure has no bearing upon the evaluation of e, discussion of it wil be postponed to another paper.

Attention may also be called to the completeness of the answers furnished by Figs. 2 and 3 to the questions raised in § 6. Thus drops No. 27 and 28 have practically identical values of $1/pa$ but while No. 28 carries, during part of the time, but 1 unit of charge (see Table XX.) drop No. 27 carries 29 times as much and it has about 7 times as large a diameter. Now if the small drop were denser than the large one (see assumption 3, § 6) or if the drag of the median upon the heavily charged drop were greater than its drag upon the one lightly charged (see assumtion 1, § 6), then for both these reasons drop 27 would move more slowly relatively to drop 28 then would otherwise be the case and hence $e_1^{\frac{3}{2}}$ for 27 would fall below $e_1^{\frac{3}{2}}$ for drop 28. Instead of this the two $e_1^{\frac{3}{2}}$'s fall so nearly together that it is impossible to represent them on the present scale by two separate dots. Drops 52 and 56 furnish an even more striking confirmation of the same conclusion, for both drops have about the same value for l/a and both are exactly on the line though No. 56

carries at one time 68 times as heavy a charge as No. 52 and has three times as large a radius. In general the fact that Figs. 2 and 3 show no tendency whatever on the part of either the very small or the very large drops to fall above or below the line is experimental proof of the joint correctness of assumptions 1, 3, and 2*b* of § 6. The correctness of 2*a* was shown by the agreement throughout Tables IV. to XIX. between $1/n'(1/t_g' - 1/t_F)$ and $1/n(1/t_g + 1/t_F)$.

The values of $e^{\frac{3}{2}}$ and b obtained graphically from the y-intercept and the slope in Fig. 2 are $e^{\frac{3}{2}} = 61.13 \times 10^{-8}$ and $b = .0006254$, p being measured, for the purposes of Fig. 2 and of this computation in mm. of Hg at 23° C. and a being measured in cm. The value of A (equations 2 and 3) corresponding to this value of B is *.874* instead of .817 as originally found. Cunningham's theory gives, in terms of the constants here used, $A = 788$.[1]

Instead however of taking the result of this graphical evaluation of $e^{\frac{3}{2}}$ it is more accurate to reduce each of the observations on $e_1^{\frac{3}{2}}$ to $e^{\frac{3}{2}}$ by means of the above value of B and the equation

$$e^{\frac{3}{2}}\left(1 + \frac{b}{pa}\right) = e_1^{\frac{3}{2}}. \qquad (14)$$

The results of this reduction are contained in the last column of Table XX. These results illustrate very clearly the sort of consistency obtained in these observations. *The largest departure from the mean value found anywhere in the table amounts to 0.5 per cent., and "the probable error" of the final mean value computed in the usual way is 16 in 61,000.*

Instead however of using this final mean value as the most reliable evaluation of $e^{\frac{3}{2}}$ it was thought preferable to make a considerable number of observations at atmospheric pressure on drops small enough to make t_g determinable with great accuracy and yet large enough so that the whole correction term to Stokes's law amounted to but a few per cent., since in this case, even, though there might be a considerable error in the correction-term constant b, such error would influence the final value of e by an inappreciable amount. The first 23 drops of Table XX. represent such observations. It will be seen that they show slightly greater consistency than do the remaining drops in the table and that the correction-term reductions for these drops all lie between 1.3 per cent. (drop No. 1) and 5.6 per cent. (drop No. 23) so that even though b were in error by as much as 3 per cent. (its error is actually not more than .5 per cent.) $e^{\frac{3}{2}}$ would be influenced by that fact to the extent of but 0.1 per cent. The mean value of $e^{\frac{3}{2}}$ obtained from the first 23 drops is 61.12×10^{-8}, a

[1] PHYS. REV., 32, p. 380; also footnote.

number which differs by 1 part in 3,400 from the mean obtained from all the drops.

When correction is made for the fact that the numbers in Table XX. were obtained on the basis of the assumption $\eta_{23} = .0001825$, instead of $\eta_{23} = .0001824$ (see § 2) the final mean value of $e^{\frac{3}{2}}$ obtained from the first 23 drops is 61.085×10^{-8}. This corresponds to

$$e = 4.774 \times 10^{-10} \text{ electrostatic units.}$$

Since the value of the Faraday constant has now been fixed virtually by international agreement[1] at 9,650 absolute electromagnetic units and since this is the number N of molecules in a gram molecule times the elementary electrical charge, we have

$$N \times 4.774 \times 10^{-10} = 9{,}650 \times 2.9990 \times 10^{10};$$

$$\therefore \quad N = 6.062 \times 10^{23}.$$

Although the probable error in this number computed by the method of least squares from Table XX. is but one part in 3,000 it would be erroneous to infer that e and N are now known with that degree of precision, for there are four constant factors entering into all of the results in Table XX. and introducing uncertainties as follows. The coefficient of viscosity η which appears in the 3/2 power introduces into e and N a maximum possible uncertainty of 0.1 per cent. The distance between the condenser plates (16.00 mm.) is correct to .01 mm., and therefore, since it appears in the 1st power in e, introduces a maximum possible error of something less than 0.1 per cent. The voltmeter readings have a maximum possible error of rather less than 0.1 per cent., and carry this in the 1st power into e and N. The cross-hair distance which is uniformly duplicatable to one part in a thousand appears in the 3/2 power and introduces an uncertainty of no more than 0.1 per cent. The other factors introduce errors which are negligible in comparison. *The uncertainty in e and N is then that due to 4 continuous factors each of which introduces a maximum possible uncertainty of 0.1 per cent.* Following the usual procedure we may estimate the uncertainty in e and N as the square root of the sum of the squares of these four uncertainties, that is, as 2 parts in 1,000. We have then finally:

$$\mathbf{e = 4.774 \pm .009 \times 10^{-10}}$$

and

$$\mathbf{N = 6.062 \pm .012 \times 10^{23}.}$$

The difference between these numbers and those originally found by the oil-drop method, viz., $e = 4.891$ and $N = 5.992$ is due to the fact

[1] Atomic weight of silver 107.88. Electrochemical equivalent of silver 0.01118.

that this much more elaborate and prolonged study has had the effect of changing every one of the three factors η, A, and d (= cross-hair distance) in such a way as to lower e and to raise N. The chief change however has been due to the elimination of the faults of the original optical system.

11. Comparison with Other Measurements.

So far as I am aware, there is at present no determination of e or N by any other method which does not involve an uncertainty at least 15 times as great as that represented in the above measurements.

Thus the *radioactive method* yields in the hands of Regener[1] a count of the α particles which gives e with an uncertainty which he estimates at 3 per cent. This is as high a precision I think as has yet been claimed for any α particle count,[2] though Geiger and Rutherford's photographic registration[3] method will doubtless be able to improve it.

The *Brownian Movement* method yields results which fluctuate between Perrin's value[4] $e = 4.24 \times 10^{-10}$, and Fletcher's value,[5] 5.01×10^{-10}, with Svedberg's measurements[6] yielding the intermediate number 4.7×10^{-10}.

The *radiation method* of Planck[7] yields N as a product of $(c_2)^3$ and σ. The latest Reichsanstalt value of c_2 is 1.436[8] while Coblentz,[9] as the result of extraordinarily careful and prolonged measurements obtains 1.4456. The difference in these two values of $(c_2)^3$ is 2 per cent. Westphal[10] estimates his error in the measurement of σ at .5 per cent. though reliable observers differ in it by 5 per cent. or 6 per cent. We may take then 3 per cent. as the limit of accuracy thus far attained in measurements of e or N by other methods. *The mean results by each one of the three other methods fall well within this limit of the value found above by the oil-drop method.*

12. Computation of Other Fundamental Constants.

For the sake of comparison and reference, the following fundamental constants are recomputed on the basis of the above measurements:

[1] Regener, Sitz. Ber. d. k. Preuss. Acad., 37, p. 948, 1909.

[2] Rutherford and Geiger, Proc. Roy. Soc., 81, p. 155, 1908.

[3] Geiger and Rutherford, Phil. Mag., 24, p. 618, 1912.

[4] J. Perrin, C. R., 152, p. 1165, 1911.

[5] H. Fletcher, PHYS. REV., 33, p. 107, 1911.

[6] Svedberg, Arkiv f. Kemi, etc., utg. af K. Sv. Vetensk. Akad., 2, 29, 1906. See also Svedberg, "Die Existenz der Mölekule," p. 136. Leipzig, 1912.

[7] Planck, Vorlesungen über die Theorie der Wärmestrahlung, 2d edition, 1913, p. 166.

[8] See Planck, Vorles., p. 163.

[9] Coblentz, Journal of the Washington Academy of Sciences, Vol. 3, p. 178, April, 1913.

[10] Wm. H. Westphal, Verh. d. D. Phys. Ges., 13, p. 987, Dec., 1912.

1. The number n of molecules in 1 c.c. of an ideal gas at 0° 76 is given by

$$n = \frac{N}{V} = \frac{6.062 \times 10^{23}}{22{,}412} = 2.705 \times 10^{19}.$$

2. The mean kinetic energy of agitation E_0 of a molecule at 0° C. is given by

$$pV = \tfrac{1}{3}Nmu^2 = \tfrac{2}{3}NE_0 = RT,$$

$$\therefore E_0 = \frac{3}{2}\frac{p_0V_0}{N} = \frac{3 \times 1{,}013{,}700 \times 22{,}412}{2 \times 6.062 \times 10^{23}} = 5.621 \times 10^{-14} \text{ ergs.}$$

3. The constant ϵ of molecular energy defined by $E_0 = \epsilon T$ is given by

$$\epsilon = \frac{E_0}{T} = \frac{5.621 \times 10^{-14}}{273.11} = 2.058 \times 10^{-16} \frac{\text{ergs}}{\text{degrees}}.$$

4. The Boltzmann entropy constant k defined by $S = k \log W$ is given by[1]

$$k = \frac{R}{N} = \frac{p_0V_0}{TN} = \tfrac{2}{3}\epsilon = 1.372 \times 10^{-16} \frac{\text{ergs}}{\text{degrees}}.$$

All of these constants are known with precisely the accuracy attained in the measurement of e.

5. The Planck "Wirkungsquantum" h can probably be obtained considerably more accurately as follows than in any other way. From equation 292, p. 166, of the "Wärmestrahlung," we obtain[2]

$$h = \frac{k^4}{c}\left(\frac{48\pi\alpha}{a}\right)^{\frac{1}{3}} = \frac{(1.372 \times 10^{-16})^4}{2.999 \times 10^{10}} \cdot \left(\frac{48\pi 1.0823}{7.39 \times 10^{-15}}\right)^{\frac{1}{3}} = 6.620 \times 10^{-27}$$

which gives h with the same accuracy attainable in the measurement of k^4/a in which a is the Stefan-Boltzmann constant. If Westphal's estimate of his error in the measurement of this constant is correct, viz., 0.5 per cent., it would introduce an uncertainty of but 0.2 per cent. into h. This is about that introduced by the above determination of k^4, hence the above value of h should not be in error by more than 0.4 per cent.

6. The constant c_2 of the Wien-Planck radiation law may also be computed with much precision from the above measurements. For also from equation 292 of the "Wärmestrahlung" we obtain

$$c_2 = \left(\frac{48\pi\alpha k}{a}\right)^{\frac{1}{3}} = \left(\frac{48\pi 1.0823\ 1.372 \times 10^{-16}}{7.39 \times 10^{-15}}\right)^{\frac{1}{3}} = 1.4470 \text{ cm. degrees.}$$

[1] See Planck's Vorles., p. 129.

[2] c = velocity of light, α = a numerical factor, and $a = 4\sigma/c$. Westphal's value of σ is 5.54×10^{-5} which corresponds to $a = 7.39 \times 10^{-15}$.

Since both k and a here appear in the 1/3 power, the error in c should be no more than 0.2 per cent., provided Westphal's error is no more than 0.5 per cent.

The difference between this and Coblentz's mean value, viz., *1.4456* is but 0.1 per cent. The agreement is then entirely satisfactory. A further independent check is found in the fact that Day and Sosman's location of the melting point of platinum at 1755° C.[1] is equivalent to a value of $c_2 = 1.4475$.[2] On the other hand, the last Reichsanstalt value of c_2, viz., 1.437, is too low to fit well with these and Westphal's measurements. It fits perfectly however with a combination of the above value of e and Shakespear's[3] value of σ, viz., $\sigma = 5.67 \times 10^{-5}$.

13. SUMMARY.

The results of this work may be summarized in the following table in which the numbers in the error column represent in the case of the first six numbers estimated limits of uncertainty rather than the so-called "probable errors" which would be much smaller. The last two constants however involve Westphal's measurements and estimates and Planck's equations as well as my own observations.

TABLE XXI.

Elementary electrical charge	$\mathbf{e = 4.774 \pm .009 \times 10^{-10}}$
Number of molecules per gram molecule	$\mathbf{N = 6.062 \pm .012 \times 10^{23}}$
Number of gas molecules per c.c. at 0° 76	$\mathbf{n = 2.705 \pm .005 \times 10^{19}}$
Kinetic energy of a molecule at 0° C	$\mathbf{E_0 = 5.621 \pm .010 \times 10^{-14}}$
Constant of molecular energy	$\mathbf{\epsilon = 2.058 \pm .004 \times 10^{-16}}$
Constant of the entropy equation	$\mathbf{k = 1.372 \pm .002 \times 10^{-16}}$
Elementary "Wirkungsquantum"	$h = 6.620 \pm .025 \times 10^{-27}$
Constant of the Wien displacement law	$c_2 = 1.4470 \pm 0030$

I take pleasure in acknowledging the able assistance of Mr. J. Yibpong Lee in making some of the above observations. Mr. Lee has also repeated with my apparatus the observations on oil at atmospheric pressure with results which are nearly as consistent as the above. Using my value of b he obtains, as a mean of measurements on 14 drops, a value of e which differs from the above by less than 1 part in 6,000, although its probable error computed as in the case of Table XX. is 1 part in 2,000.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
June 2, 1913.

[1] Amer. Jour. Sci., 30, p. 3, 1910.
[2] Coblentz, Journal of the Washington Academy of Sciences, Vol. 3, p. 13.
[3] G. A. Shakespear, Proc. Roy. Soc., 86, 180, 1911.

THE EMISSIVITY OF OXIDIZED METALLIC SURFACES.[1]

BY C. P. RANDOLPH AND M. J. OVERHOLSER.

THE measurements here described were undertaken to secure data on the total radiation from oxidized metallic surfaces, at temperatures below 700° C. Total radiation includes all the energy dissipated from a surface by radiation, at wave-lengths from 0 to ∞. A large amount of accurate work on selective radiation is available, but comparatively little on total radiation. Data on the latter are necessary when dealing with heat losses from surfaces.

The emissivity of a body is here defined as the ratio of the energy radiated by a body of emissivity e, to the energy radiated by a black body, when both are at the same temperature. This is not the definition always used,[2] but it is the most convenient for comparing different surfaces when dealing with total radiation.[3] A "black body" is, of course, one that absorbs all the radiation incident upon it, no matter what the wave-length. From the Stefan-Boltzman law, for a black body

$$W = \sigma(T_1^4 - T_2^4),$$

where W is the rate of heat loss, σ is a constant experimentally determined, and T_1 and T_2 are the absolute temperatures respectively of the radiating surface and of the surroundings. Then for a body of emissivity e,

$$W = e\sigma(T_1^4 - T_2^4).$$

The construction of the apparatus used for comparing the radiation from various surfaces with that from a black body is shown in Figs. 1 and 2. It was our aim to construct a robust instrument that could be used in connection with a Leeds and Northrup potentiometer (read accurately to .001 millivolt), thus making it unnecessary to observe galvanometer deflections. Of course there are many radiometers far more delicate than this.

The absorbing disc A (Fig. 1) is of platinum .25 mm. thick, coated with platinum-black on the side presented to the radiating surface. It is supported by three wires (one is shown at K), .25 mm. diameter, and

[1] From the heating device research laboratory, General Electric Company.

[2] Preston's Theory of Heat, 2d ed., 587.

[3] Poynting and Thompson's Heat, 233.

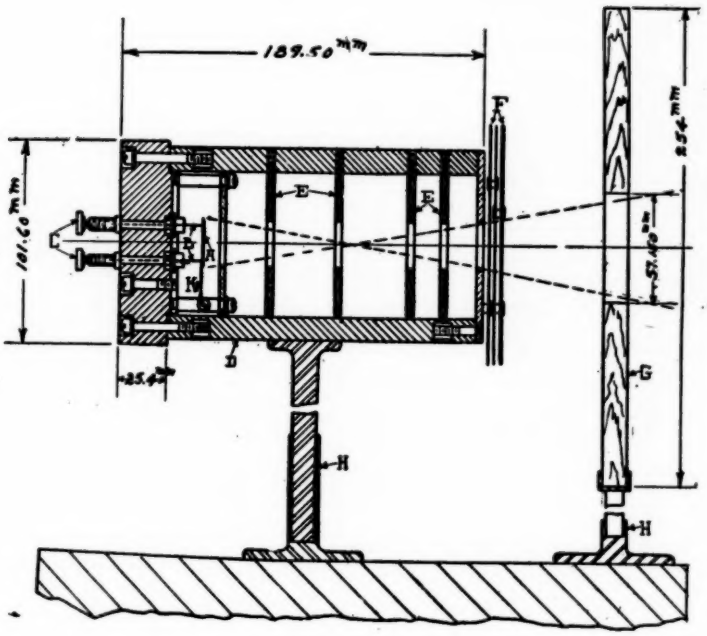

Fig. 1.

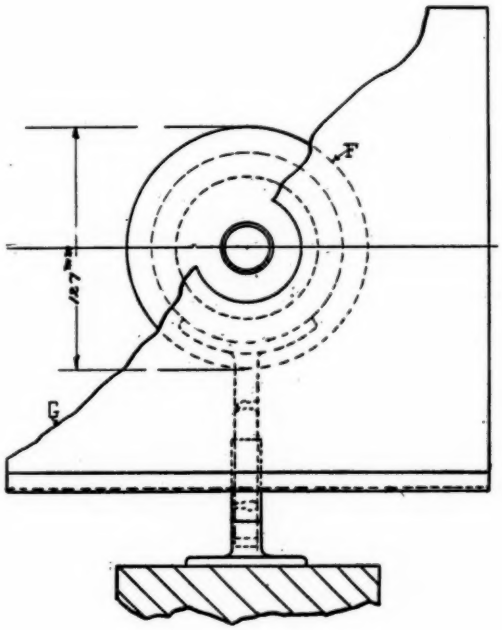

Fig. 2.

to the disc is soldered (on the polished side) a bismuth-iron thermo-couple *B*. The cold junctions of the thermo-couple are brought out to the binding posts *C*, which are always at room temperature. The walls *D* are of hard rubber, so thick that they can heat very slightly in the short time the instrument is exposed to a radiating surface for a measurement. Baffles *EE*, also of black hard rubber, prevent any heating of the absorber *A* by convection, and also prevent reflection of radiant heat from the walls *D* to the absorber. Three thin brass discs *F* protect the end wall *G* from being heated by the radiating surface. It was found necessary also to protect the side walls from radiation by placing a square wooden shield *G* between the radiometer and the radiating surface. This shield is somewhat larger than any of the radiating surfaces used in the measurements,

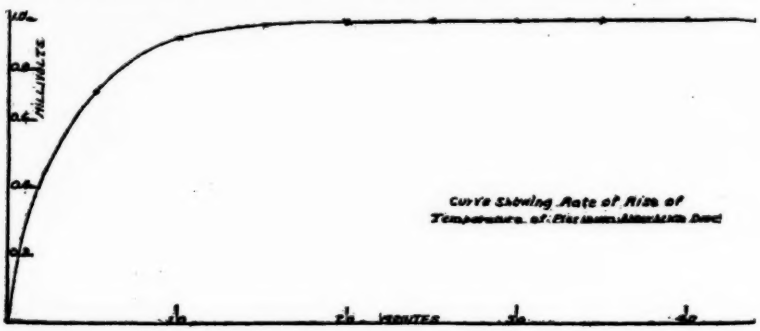

Fig. 3.

and is painted black on the side away from the radiometer to reduce reflection to a minimum. The cylinder *D* and the shield *G* are supported by brass rods fitting in tubes *HH* and can be adjusted at any height with thumb screws.

The curve in Fig. 3 for the rate of rise of temperature of the platinum absorber shows that it reaches a maximum temperature three minutes after exposure. All readings were taken after an exposure of four minutes, to make sure that the horizontal part of the curve had been reached. No lenses or reflectors are used in the design of the radiometer, and therefore the only chance of error from selective absorption is that the platinum absorber itself might possess this property. But platinum-black comes very close to being a black body, so that the possibility of error here is very slight.

The radiation through a relatively small opening in a closed uniform temperature surface has been shown to be black-body radiation, no matter what the material of the surface may be.[1] This fact was made use of in

[1] Balfour Stewart, Lessons in Elementary Physics.

calibrating the radiometer. Fig. 4 shows the "black body." *A* is a large cast-iron pipe, closed at the rear with another heavy casting *B*. The pipe and the casting *B* are heated by three "calorite" wire resistors *CC* so connected that the energy dissipated by each heating unit can be adjusted independently. The temperature is thus kept very uniform. Five thermo-couples *DD* were used for measuring the temperature, which could be kept uniform within 3° C. at 500° C. The iron castings were surrounded with insulation, as shown, which reduces the energy necessary for maintaining any temperature, and makes it easier to maintain a uniform temperature. A water jacket *E* prevents the outher wall from heat-

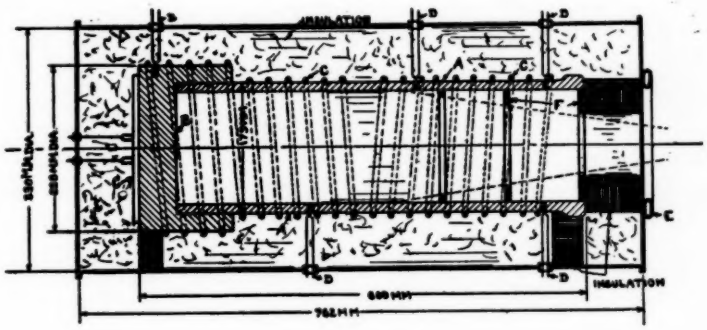

Fig. 4.

ing at the end. The baffles *FF* make the inner surface approximate more closely to an entirely closed surface, thus reducing to a minimum the difference between the radiation from the casting and that from a perfectly black body.

The rate at which energy was radiated from the black body was calculated from its observed temperatures and the temperature of the surroundings, by substituting in the Stefan-Boltzman equation. A calibration curve was plotted for the radiometer showing the relation between millivolts and energy radiated. The temperature of the surroundings was taken as 25° C., in all measurements. Where the radiating surface is at a temperature above about 175° C., a change in the room temperature of a few degrees can easily be shown to introduce only a negligible error.

Since

$$e \equiv \frac{e\sigma(T_1^4 - T_2^4)}{\sigma(T_1^4 - T_2^4)}$$

the value of σ does not affect the results and temperature errors also correct themselves to a certain extent. The platinum-platinum-iridium

thermo-couples used for measuring the temperatures of the black body and of the oxidized surfaces were calibrated under exactly the same conditions.

A metal disc 19.1 cm. diameter and 6 mm. to 13 mm. thick, mounted vertically, with its exposed surface flush with the end of a horizontal iron cylinder (the axis of the disc and the cylinder coinciding) formed the radiating surface of which the emissivities were measured.[1] The heating unit was made of a calorite resistance ribbon between two mica discs. This unit was clamped between the radiating disc and a thin disc of sheet steel. The cylinder back of the 19 cm. disc was filled with good heat insulating material, thus decreasing the energy necessary to maintain the radiating disc at any temperature. The thermo-couple was held firmly against the back of the disc under the head of a screw, the two leads being brought out to the cold junction (kept in oil) through the heat insulation. There was a space of about 19 mm. between the edges of the disc and the inside of the cylinder walls which was also filled with insulation, held in place with a mica ring. The surface of each disc was cleaned and polished before it was mounted.

The thermo-couple measures the temperature of the back of the metal disc and not that of the radiating surface itself. In some cases—as with copper and other good heat conductors—this drop in temperature between the two surfaces of the disc is negligible. With poor heat conductors—as certain alloys—it is very important to make a correction at higher temperatures. We had previously accurately measured the thermal conductivity at various temperatures of nearly all the metals or alloys used in these experiments, and for those which we had not measured ourselves the values were obtained from the literature.[2] The wattmeter readings gave the total energy required to maintain a surface at any temperature. The watts per square centimeter lost from the surfaces by radiation and convection was calculated by subtracting the heat conducted through the insulation, from the wattmeter reading. Then the actual temperature of the radiating surface is

$$T_1 = t - WRL,$$

where t is the temperature as measured with the thermo-couple, W is the heat flux through the metal disc, R is the thermal resistivity of the metal and L is the thickness of the plate. As this correction is in all cases rela-

[1] The method of mounting the metal plate is fully described with drawings by I. Langmuir in J. Am. Elec. Soc., XXIII., 14 (1913).

[2] Jaeger and Disselhorst, Wiss. Abh. d. Phys. Techn. Reichanst., 3, 269 (1900); Angell, PHYS. REV., XXXIII., 421 (1911).

tively small, any possible error in it becomes negligible in the final results. With the type of heating unit used, the thickness of the plate was always made great enough to insure a very uniform temperature over its surface.

We found on beginning the measurements given below that the emis-

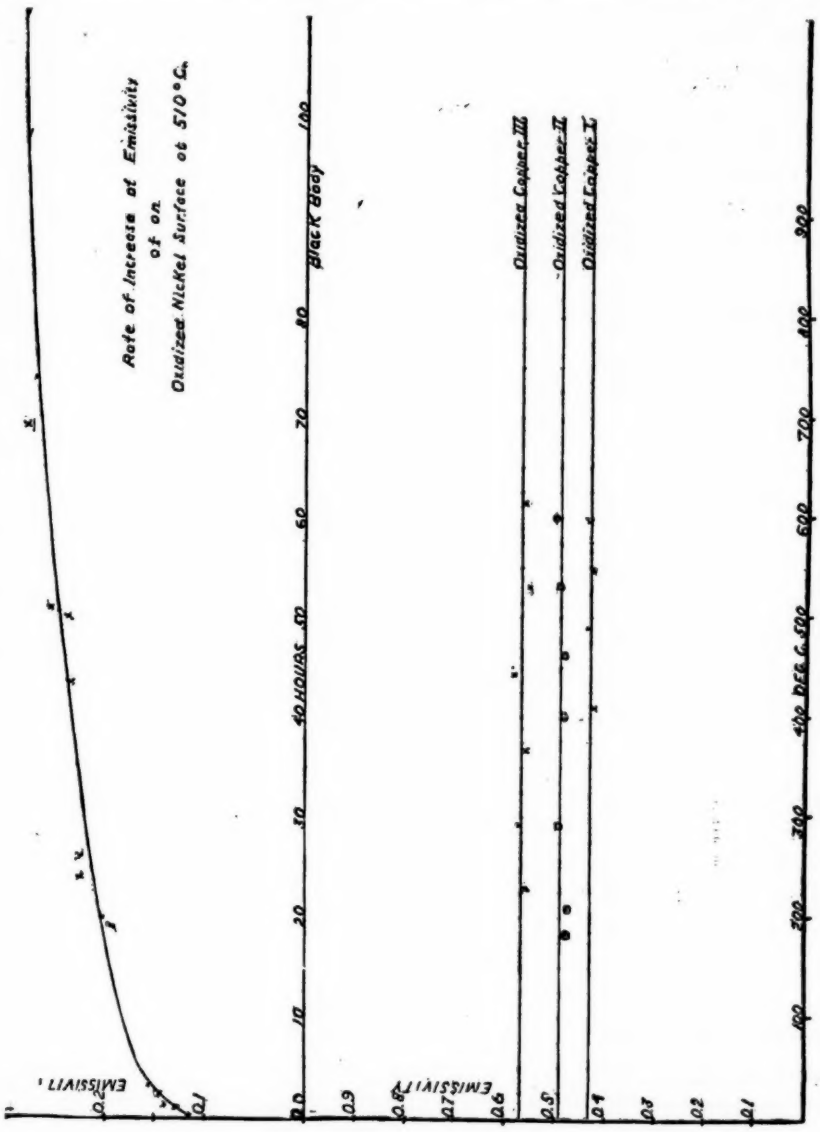

Fig. 5.

sivity increases (1) with the temperature to which the surface has presivity of a surface depends on the depth of oxidation; that is, the emis-

viously been heated and (2) with the time the surface is kept at any temperature. In Fig. 5 is shown the rate of increase of the emissivity of an oxidized nickel surface at 510° C. Zero time is here taken as the time when we could get the first measurement after the surface had been quickly heated to 510° C., starting with a polished surface. The constant value is seen to be .283. The temperature was then increased to 583°, where the constant value of the emissivity was .410. In Fig. 6 it is seen that the maximum emissivity is .49, when the surface is heated to 640° C. With the exception of the oxidized copper surface, in all the measurements made, the method was to start with a polished surface which was kept at the maximum temperature for which a point is given on the curves, until the emissivity had become constant. Measurements were then taken at various lower temperatures.

Fig. 5 shows a series of measurements at different temperatures for oxidized copper. Curves I. and II. were determined by measuring the

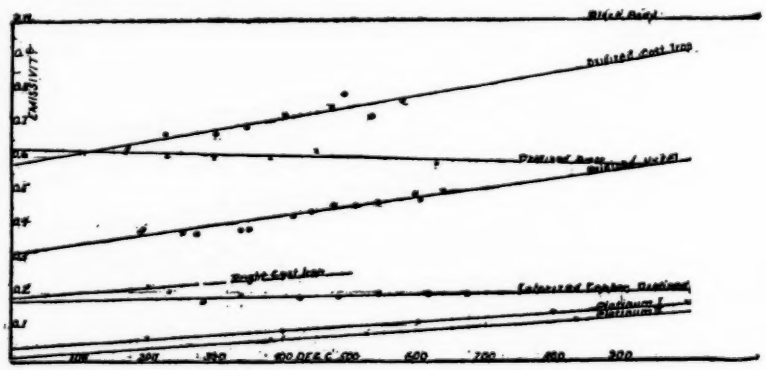

Fig. 6.

emissivity before it had become constant at the maximum temperatures for which results are given. Then observations were taken at various lower temperatures as explained above. Curve III. was obtained in the usual way, by heating the surface at the maximum temperature until the radiation was constant. It is seen that if a copper surface is heated for even a *very short time* at a temperature *A* about 50° higher than temperature *B*, the emissivity has reached or passed the maximum value it would attain if the surface had been kept at *B* indefinitely.

The curves for calorized copper and calorized steel (Figs. 6 and 7) refer to plates of the above metals which have been impregnated with aluminum in their surfaces. This process requires that they be heated to a temperature above that at which measurements were made, so that we would expect no variation of emissivity with time of heating. This agrees with the experimental results.

The emissivities of platinum and silver (Figs. 6 and 7) are taken from the literature, and are given here for comparison. The values for silver and platinum I. are calculated from Hagen and Ruben's formula[1] for long wave-length radiation:

$$e = .365\frac{r}{\lambda},$$

where e = emissivity,

r = electrical resistivity in ohms per cm³,

λ = wave-length of radiant energy in cm.

λ is determined by Wien's law, which gives the relation between the

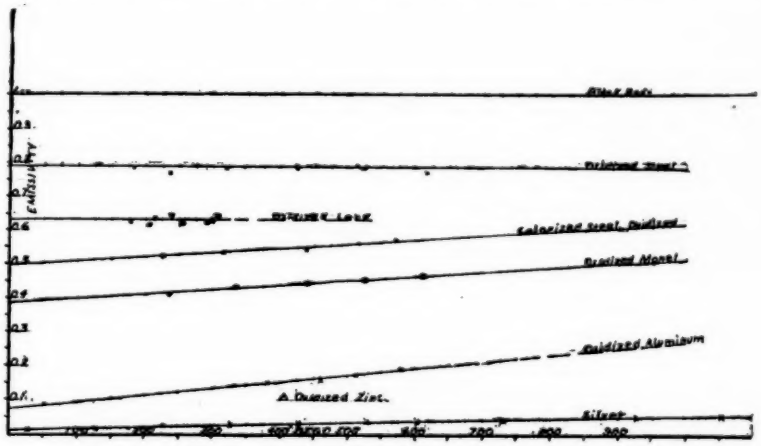

Fig. 7.

absolute temperature T and the wave-length of maximum intensity, viz.,

$$\lambda_m = \frac{.290}{T} \text{ cm.}$$

For the sample of silver for which the emissivity is here calculated, $r = 1.76 \times 10^{-6}$ at 0° C. Jaeger and Disselhorst[2] found the temperature coefficient of the electrical resistivity of silver to be .0040. Therefore

$$e = .61 \times 10^{-3}\sqrt{T(1+.0040T)}.$$

Platinum I. is a sample used by I. Langmuir in measuring convection losses.[3] He measured the electrical resistivity at various temperatures, and the emissivity is calculated from these results as for silver. The

[1] Hagen and Ruben's Ann. Phys., 8, 1 (1902).

[2] Jaeger and Disselhorst, Phys. Tech. Reich., 3, 269 (1900).

[3] I. Langmuir, PHYS. REV., XXXIV., 401 (1912).

curve platinum II. is taken from actual measurements of emissivity by Lummer and Kurlbaum.[1]

The values of emissivities in the following table are taken from the curves and are given here for convenience.

	Temperature, Deg. C.		
	200	400	600
Silver	.020	.030	.038
Platinum (1)	.060	.086	.110
Oxidized zinc	——	.110	——
Oxidized aluminum	.113	.153	.192
Calorized copper, oxidized	.180	.185	.190
Cast iron	.210	——	——
Oxidized nickel	.369	.424	.478
Oxidized monel	.411	.439	.463
Calorized steel, oxidized	.521	.547	.570
Oxidized copper	.568	.568	.568
Oxidized brass	.610	.600	.589
Oxidized lead	.631	——	——
Oxidized cast iron	.643	.710	.777
Oxidized steel	.790	.788	.787
Black body	1.00	1.00	1.00

CONCLUSIONS.

1. The emissivity of an oxidized metallic surface depends on the depth of the surface oxidation. Therefore it is a function (*a*) of the temperature to which the surface has previously been heated and (*b*) of the time the surface has been maintained at the temperature.

2. The emissivities of certain surfaces have been measured at various temperatures and the results are given here. The surfaces were oxidized at about 600° (the temperature of oxidation is always the highest shown on the temperature-emissivity curves) until the emissivity had become constant.

3. It is possible that the variations so often found in scientific literature in measurements of heat losses from surfaces are due to changes in the radiation and not to unsteady convection losses.

[1] Lummer and Kurlbaum, Verh. Phys., Ges., Berlin, 17, 106 (1898).

THE ACTION OF MERCURY VAPOR ON SELENIUM.

BY F. C. BROWN.

PREVIOUSLY[1] I have shown that all the known changes of conductivity of selenium with the time of exposure to light can be explained mathematically by assuming a dynamic equilibrium between three components A, B and C. But in this analysis there appeared on obvious physical interpretation of the varying initial rates of change which were imposed on the different varieties of selenium for equilibrium in the dark. This fact has led the author to search for the conditions which will consistently and certainly produce one of the varieties of selenium about which there is most dispute, viz., light-negative selenium. The question as to whether the light-negative property is in the selenium itself or is in impurities, or selenium compounds, was one that had to be definitely settled. While the search has not answered all questions that have arisen, it has proved worth while in that it has resulted in some definite advances, that are interesting and which further limit future investigations. It is found that mercury vapor will uniformly transform different allotropic modifications of selenium into light-negative selenium, and further that the mercury vapor probably forms chemical union with the selenium.

In considering a relationship which I observed between the conductivity of selenium and its sensibility, viz., that light-negative selenium is associated with high conductivity, it occurred to me that any method that produces low resistance selenium might also at the same time produce light-negative selenium. In this connection it was noted that Moss[2] and later Minchin[3] had observed the remarkable decrease of resistance of selenium when it was placed in a vacuum produced by a mercury pump. Moss first exposed a bar of vitreous selenium to mercury vapor in a partial vacuum, whereupon he observed that the conductivity increased to a higher value than that of any known modification of selenium. He attributed this conductivity to a mercury film, and consequently it is not surprising that he overlooked the negative action of light. Minchin placed a light-positive selenium cell in a Sprengel vacuum. He observed that cells of several hundred thousand ohms decreased in resistance in

[1] PHYS. REV., 33, pp. 1 and 403.

[2] Phil. Mag., Ser. 5, 3, p. 67, 1877.

[3] Nature, 77, p. 198 and p. 222, 1908.

three or four days to values as low as 50 ohms, but he did not observe any light sensitiveness after the low resistance was reached.

THE CRYSTALLIZATION OF SELENIUM IN AN ATMOSPHERE IN WHICH MERCURY VAPOR IS PRESENT.

The first experiments that exhibited the action of mercury vapor on selenium were those in which the selenium in an ordinary cell form was crystallized in the presence of mercury vapor in air. The cell form consisted of two parallel wires wound around a porcelain cleat such as is used by the electrician for holding and insulating wires. The selenium was first melted on this cleat and then undercooled, thus giving the vitreous allotrope attached to the wires. This selenium form was then placed just over a heating bath of quartz sand. At the bottom of the sand was a globule of mercury. The bath was heated by a bunsen burner from below, and consequently the temperature of the mercury was much higher than that of the selenium. It was found that if the selenium was kept anywhere between 150° and 200°, its conductivity reached a very high value, which it maintained after cooling to room temperature. Immediately upon cooling the selenium displayed light-negative characteristics, *i. e.*, the conductivity decreased when the cell was illuminated.

It seems that the mercury diffused up through the sand and condensed on the selenium. As might be expected the higher the temperature of the sand bath and of the selenium, the sooner did the selenium reach an approximately constant high conductivity. If the selenium were kept at about 190° for about 10 minutes, the resistance of the cell would drop to about 20 ohms, while if the temperature were kept at 150° several hours were required in order that this conductivity might be attained. No differences in the light-characteristics could be detected by varying the temperatures within the range noted. However if the selenium were heated below 140° or above 200°, the light sensitiveness did not appear. Perhaps at the lower temperature an appreciable amount of the mercury vapor did not reach the selenium while at the higher temperatures an explanation must probably involve chemical union of the selenium and mercury or special allotropic modification of the selenium. Some thirty samples were made in this way, with but the use of a single drop of mercury in the sand bath.

The characteristics of the light-negative selenium prepared in this manner were not investigated fully, but many of them behaved much like the specimen described by Miss Crum.[1] Aside from the light-

[1] PHYS. REV., 33, 538, 1911.

negative character, the irregularities and the lack of permanency were the most striking peculiarities. Frequently the resistance would take sudden jumps, particularly if the specimen was illuminated or jarred. Occasionally the selenium would be light-negative with faint illumination but light-positive with intense illumination, and even more frequently a specimen would temporarily change over from light-negative to light-positive character. At one time as many as one fourth of the samples in my possession were light-positive when tested with light of uniform intensity. Frequently the sensibility was quite great. One sample changed from 74.6 ohms in the dark to 104.0 ohms in the light. It maintained an average sensibility half as large for about a week. The irregularity of one sample is illustrated by the following readings taken with the selenium alternately in the dark and in the light, at intervals of about two minutes.

Resistance in Dark.	Resistance in Light.
100	117
100	101.5
98.8	105.0
95	

Not all the samples made in this way were permanent. The maximum change of resistance by light was probably greatest about two days after manufacture. After that time the sensibility gradually decreased until finally after a month there was almost no effect due to light action.

It was considered possible so far as the above experiment decides that the mercury vapor may have acted in any one of three ways. The mercury may have acted chemically on the selenium so as to form a selenide, it may have acted catalytically in a way to alter the equilibrium of the selenium components, or it may have been merely entrapped in the selenium, without otherwise essentially altering its electrical properties.

One basis for the belief in the formation of a selenide at this stage of the experimenting lay in the statement, in Watt's Dictionary of Chemistry, that mercuric selenide is formed when mercury and selenium are heated together. However I noted that mercury did not freely combine with selenium, even when the latter was heated to its melting point.

If the mercury were trapped in the selenium by some absorption process so as to form a kind of solid solution, we would at once have an explanation of the high conductivity that always accompanies this light-negative property. Perhaps the light action merely alters the form of the crystals in all varieties of selenium similarly, and in this light-negative variety it thereby breaks the conducting film of mercury. This is a simple and apparently satisfactory explanation. It readily accounts for the irreg-

ularity and non-uniform behavior of the new selenium form. However it does not explain why light-negative selenium should be produced in the presence of mercury vapor, under conditions that would not produce any light sensibility at all in the absence of mercury vapor.

Should the mercury vapor act catalytically, so as to alter the rates of change of the existent components in the selenium, we have at once a satisfactory explanation. The first difficulty in the way of this explanation is the possible formation of a selenide. More will be said later concerning these theories.

THE EFFECT OF UNHEATED MERCURY VAPOR ON LIGHT-POSITIVE SELENIUM.

There was considerable uncertainty in the last experiment as to whether the mercury vapor at the high temperature may not have acted on selenium by chemical union. If such chemical action did not take place then it seemed reasonable to hope that mercury vapor at room temperatures might transform light-positive selenium into light-negative selenium. This is particularly consistent with the view that in the light-negative selenium the conducting material is essentially mercury, which is broken and altered by the selenium crystals changing form under the action of light.

Accordingly two small cells, made by dividing a regular size Giltay cell into parts, were placed in an apparatus connecting with a Gaede vacuum pump. The resistance of each sample was upwards of twenty million ohms, in the dark, and possessed the usual sensibility to light. After being kept in a vacuum of less than .01 mm. for twenty minutes there was no apparent change in resistance, but after being in the vacuum for twelve hours the resistance had fallen to 40 ohms. At first the irregularity of behavior when illuminated resembled that of the light-negative samples previously described. The resistance was so unsteady that it was difficult to say just what action was due to the light. The cell was then placed in a kerosene bath. After resting thus for several hours, it showed consistent light-negative properties. The following is a sample of the observations taken with the selenium alternately in the dark and illuminated with a 16 c.p. lamp at 20 cm. distance.

Resistance in Dark.	Resistance in Light.
70.5	70.6
70.5	70.61
70.5	70.58
70.5	70.56
71.3	71.5

And after resting three months in the dark, the behavior is illustrated by these readings. The illumination was approximately that above.

Resistance in Dark.	Resistance in Light.
86.3	86.43
86.33	86.43
86.33	86.50
86.0	86.12
86.0	86.11

The curve in Fig. 1 shows the manner in which the resistance changes with the time of exposure. The rate of change is not nearly so rapid as that of a light-negative sample for which the curve is given in Fig. 9 of a former paper on the "Nature of Light-action in Selenium."[1]

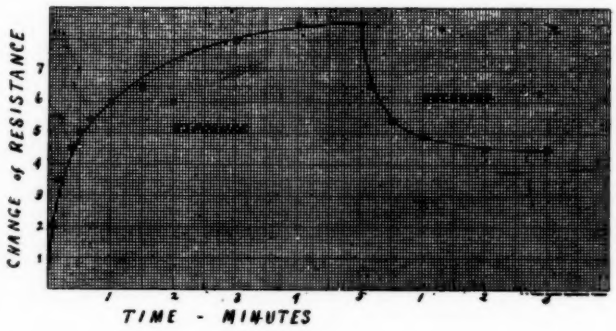

Fig. 1.

The difference in these two may be accounted for by the unequal light intensity in the two instances. At any rate the resistance begins to decrease at the instant of illumination in these new samples, and the change is so rapid at first that it is quite improbable that it is due to heat rather than light action. To definitely determine this point I hope soon to be able to map the sensibility of this variety of selenium throughout the spectrum, as Pfund[2] has done for light-positive selenium. Such a determination may also aid in a physical interpretation of the nature of the change of resistance.

The second sample referred to above was weighed before and after exposing it to the mercury vapor, to detect if possible the amount of mercury that was necessary to perform the observed transformation. Before placing in a vacuum and while the resistance was several million ohms the weight was 1.2527 gm. After exposing to mercury vapor in a partial vacuum for 16 hours, the resistance fell to 104 ohms. The

[1] PHYS. REV., 33, p. 19.
[2] PHYS. REV., 34, p. 370, 1912.

weight had not changed by as much as 0.1 milligram. This result is not inconsistent with the supposition that the increase of conductivity arises solely from the direct conductance of the absorbed mercury vapor. For if it is assumed that the mercury vapor has the same conducting power as large masses of mercury, it can be readily calculated that a film of mercury 2.5×10^{-9} cm. thick would have been sufficient to account for the observed conductivity. Further the weight of such a film would be only 1.2×10^{-8} gm., which amount it would be impossible to detect by weighing. But even with this small amount of mercury inside the selenium the concentration of mercury would be about a billion times as dense as that in a saturated free space at the same temperature.

THE ACTION ON POWDERED RED AMORPHOUS SELENIUM.

If in the Giltay cell, we could have been certain that all the selenium was acted upon, we would have known by the absence of increased weight that no chemical action took place. But as there was no obvious change of color or appearance, no estimate could be made of the extent of action of the mercury vapor.

The red amorphous selenium was exposed to the mercury vapor in a vacuum with the hope that a change in color would indicate the extent of the action. First a very small fraction of a gram of the red powder was scattered in the vacuum tube. Within half an hour after high vacuum was reached this selenium had turned black. The selenium was then packed between two wire electrodes. The resistance was fairly steady at 240 ohms. It was also light-negative, showing an increase of from 0.5 to 20 ohms. After heating for thirty minutes at 210° the resistance was reduced to 1.2 ohms. For a week following this heating the resistance was unsteady and slowly increased in value. However it did become steady after this interval and it was then quite light-sensitive. Several light-negative samples were made by packing this black selenium between wire electrodes. They were all of very low resistance and light-negative in character.

The fact that the red amorphous form did change its color to a distinct black, made it seem apparent that chemical action did not take place. If mercury selenide were formed, then when all the selenium changed to the black form it should increase in weight by the ratio of 79 to 200.

TWO SAMPLES OF RED SELENIUM WERE WEIGHED AS FOLLOWS:

Test No. 1.

Weight of glass tube container	1.066 gm.
Container + selenium	1.661
In vacuum 4 hours, 90 per cent. black	1.674
In vacuum 12 hours	1.667
In vacuum 10 hours longer	1.660

Test No. 2.

Weight of paper	0.514 gm.	
Paper + red amorphous selenium.	.808	
After 4 hours exposure to vapor	.803	
After 12 hours longer exposure	.803	
Exposure continued 6 hours	.808	selenium almost entirely black.
Exposure continued 4 hours	.797	mercury heated slightly.
Exposed to air 16 hours	.815	
Exposed 10 hours longer in vacuum	.801	
Exposed to air 3 hours	.813	

A third test was made using 2.013 grams of selenium. After exposure for about 60 hours the selenium was mostly blackened, and the weight had increased to only 2.033 grams. During exposure the effect of the mercury vapor did not penetrate far into the mass of powder. It was seldom blackened deeper than a millimeter, so that it was necessary to frequently stir a fresh surface for exposure. The second test showed what seemed to be the hygroscopic property of the selenium, by an increase in weight when it was exposed to the air. The fact that the selenium is blackened only near the surface, leads to the belief that the absorbed moisture does not play a very important part in the transformation.

The figures in these three tests apparently demonstrate that chemical combination between the selenium and the mercury vapor is quite inconceivable. If there were any definite measurable increase of weight due to the absorption of mercury vapor, it is masked by the variations in weight due to moisture and uncertain causes.

However I was deceived here by assuming that because the selenium was blackened in from 4 to 60 hours, and increased in weight by less than .03 gram that there could be no further action between the mercury and the selenium. The truth is that while it was blackened it was not all acted upon. After being exposed 1,230 hours in a high vacuum a sample weighing 0.565 gram increased in weight to 1.803 grams. When the vacuum was kept at the X-ray stage the increase was almost uniformly one milligram per hour for the first 1,000 hours, but during the next 200 hours, the weight increased more and more slowly. If mercuric selenide were formed the weight should have ultimately increased to 1.995 grams. The fact that this weight was not quite reached can easily be explained by the loss of selenium during weighings and by diffusion of its vapor in high vacuum, if not to the fact that sufficient time was not allowed for complete penetration and action.

I do not believe it right to assume at this time that the mercury vapor in a finely divided state in the selenium can have these light-negative

properties, except for the action of light on selenium or the selenium compound.

One determination of the density of this new selenium gave 4.98, but this particular sample may have had some free mercury with it. With my arrangements it is a slow process to produce a sufficiently large quantity for an accurate determination of the density. A globule of mercury acts very rapidly on selenium surrounding it in a vacuum but at atmospheric pressure a mercury globule in contact with the red powder will not perceptibly color the selenium in several days. Later I hope to obtain the density more accurately. It will probably show the same density as mercuric selenide, which in fact it resembles.

It may be mentioned that powdered vitreous selenium when placed in an atmosphere of mercury vapor for 18 hours also assumes a high conductivity and the light-negative property. There is no apparent change in the color of this modification. It is rather strange that any powder should have such a high conductivity when rather loosely packed as the powders here were packed. The interaction between the mercury and the selenium arises probably more essentially from a property of the selenium. Powdered sulphur when exposed several days to mercury vapor at the same time the selenium was exposed showed no conductivity at all.

SUMMARY.

1. Mercury vapor acts on selenium in such a manner as to produce a very high conductivity and the light-negative property.

2. The mercury acts on the amorphous form and probably also on the other modifications so as to produce selenium of new characteristics. Permanent chemical compounds are probably formed between the mercury and the selenium.

3. A very easy and satisfactory method of making light-negative selenium cells is to place the amorphous selenium in a mercury vacuum until it becomes black, and then to press this black selenium between fixed electrodes.

4. The energy curve should be mapped out in order to gain evidence as to the similarity of action of light in this and light-positive selenium.

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